

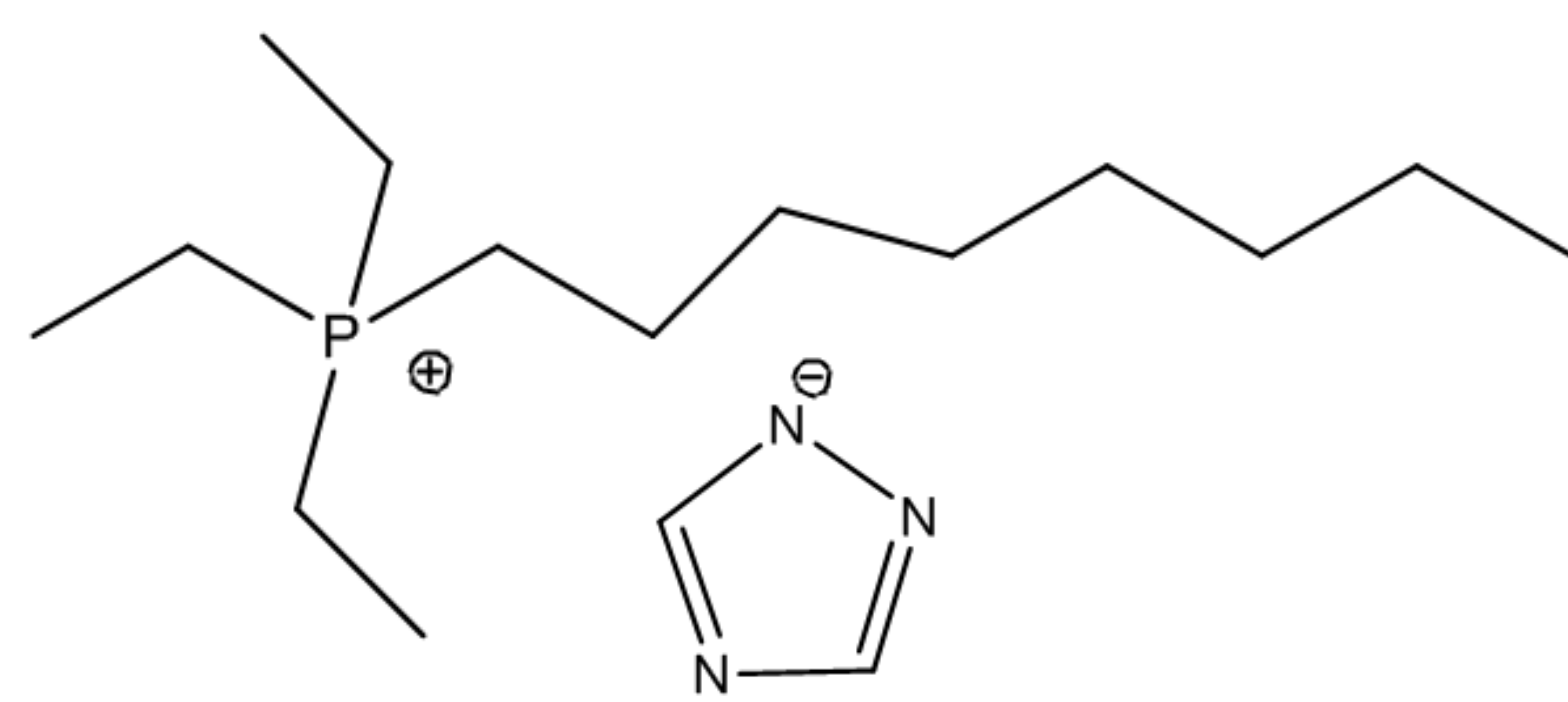
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Objective

The ion-ion and ion-solvent interactions within solutions with various mol fractions of the ionic liquid (IL) triethyl(octyl)phosphonium 1,2,4-triazol-1-ide ($[P_{2228}][4\text{-triaz}][4\text{-triaz}]$) dissolved in the acetonitrile were investigated.

Motivation

The unique electrochemical and physiochemical properties of ILs make them potential candidates for greener and safer agents to be used in the capture of post-combustion carbon dioxide (CO_2) from coal-burning power plants, as well as a viable replacement for the toxic electrolyte solutions conventionally used in batteries. $[P_{2228}][4\text{-triaz}]$ shows promise as an effective agent for the chemical absorption of CO_2 because $[P_{2228}]$ is relatively inert to CO_2 , while the available amine groups on the $[4\text{-triaz}]$ allow it, theoretically, to achieve a 1:1 reaction stoichiometry when binding CO_2 .



In practice, however, it remains difficult to achieve a 1:1 reaction stoichiometry between CO_2 and $[4\text{-triaz}]$. The ability of the amine groups on $[4\text{-triaz}]$ to bind CO_2 is hindered by the hydrogen bonding that occurs between the acidic alpha protons on the cation and the nitrogens on the anion. Dissolving the IL in the polar aprotic solvent acetonitrile may limit the hydrogen bonding between the ions and increase ion dissociation, which would improve the stoichiometric efficiency of the absorption of CO_2 by the amine groups on the $[4\text{-triaz}]$.¹

Materials and Methods

$[P_{2228}][4\text{-triaz}]$ was synthesized and dried under a vacuum for 48 hours. Solutions of ~4.3 g of $[P_{2228}][4\text{-triaz}]$ and acetonitrile were prepared in a nitrogen atmosphere (Figure 1) at the following mol fracs of IL: 0.01, 0.02, 0.05, 0.075, 0.10, 0.20 and 0.40.² The density, viscosity, and electrical conductivity (see Figure 2, 3, and 4) of each solution were measured at temperatures of 22°C, 25°C, 30°C, 40°C, 50°C, and 60°C. The water content of each solution before and after each measurement was below 1000 ppm.

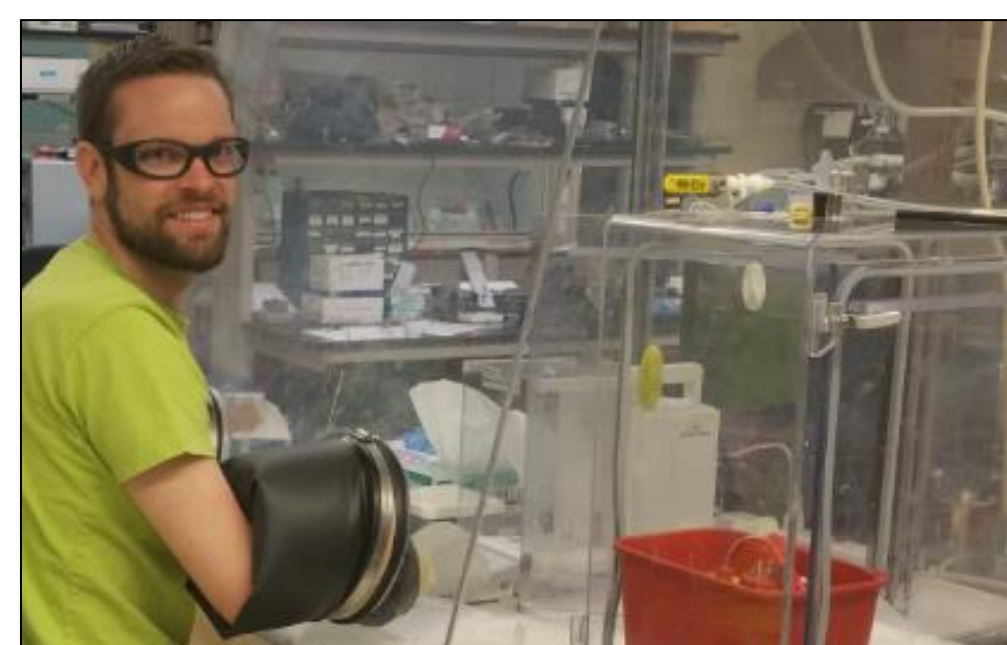


Figure 1. Preparation of solutions in a glove box with a nitrogen atmosphere.



Figure 2. DMA 4500 Anton Paar oscillating U-tube densitometer.

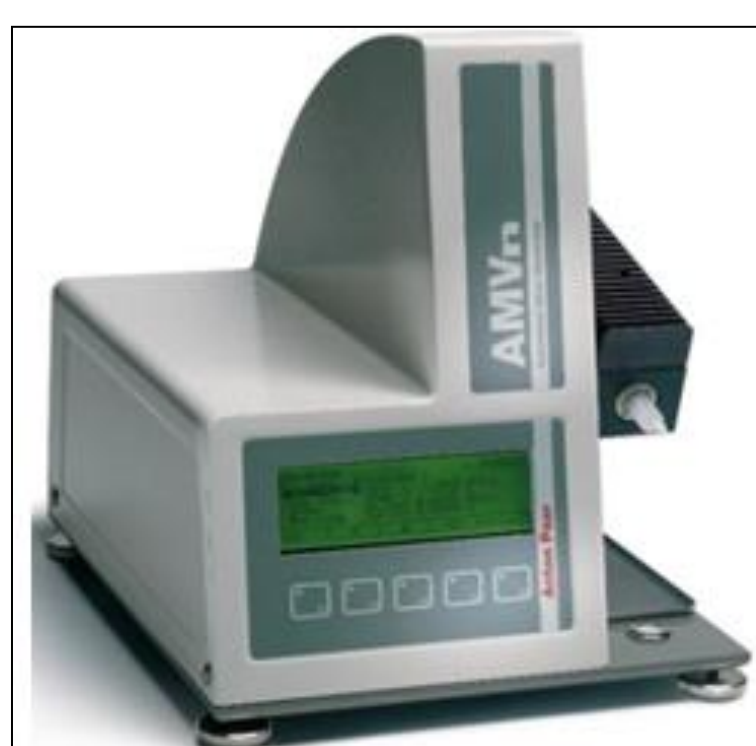


Figure 3. Anton Paar microviscosimeter.



Figure 4. Solartron electrochemical impedance interface.

Results

A Walden plot quantifies the relationship between molar conductivity per mol frac of IL (Λ , $S\text{-cm}^2\text{mol}^{-1}$) and the inverse of the viscosity (η , Poise^{-1}), also known as the fluidity of the solution. From the Walden plot (Figure 5), graphed on a logarithmic scale, equation 1 was used to derive the % ionicity (Figure 6) for each mol frac of $[P_{2228}][4\text{-triaz}]$.

$$\% \text{ ionicity} = 10^{(-\Delta W)} \times 100 \quad (1)^3$$

where ΔW is the distance between the plotted solution and the ideal dissociation of 1M KCl. The electrical conductivity (Figure 7) and viscosity (Figure 8) were also measured for each mol frac of $[P_{2228}][4\text{-triaz}]$.

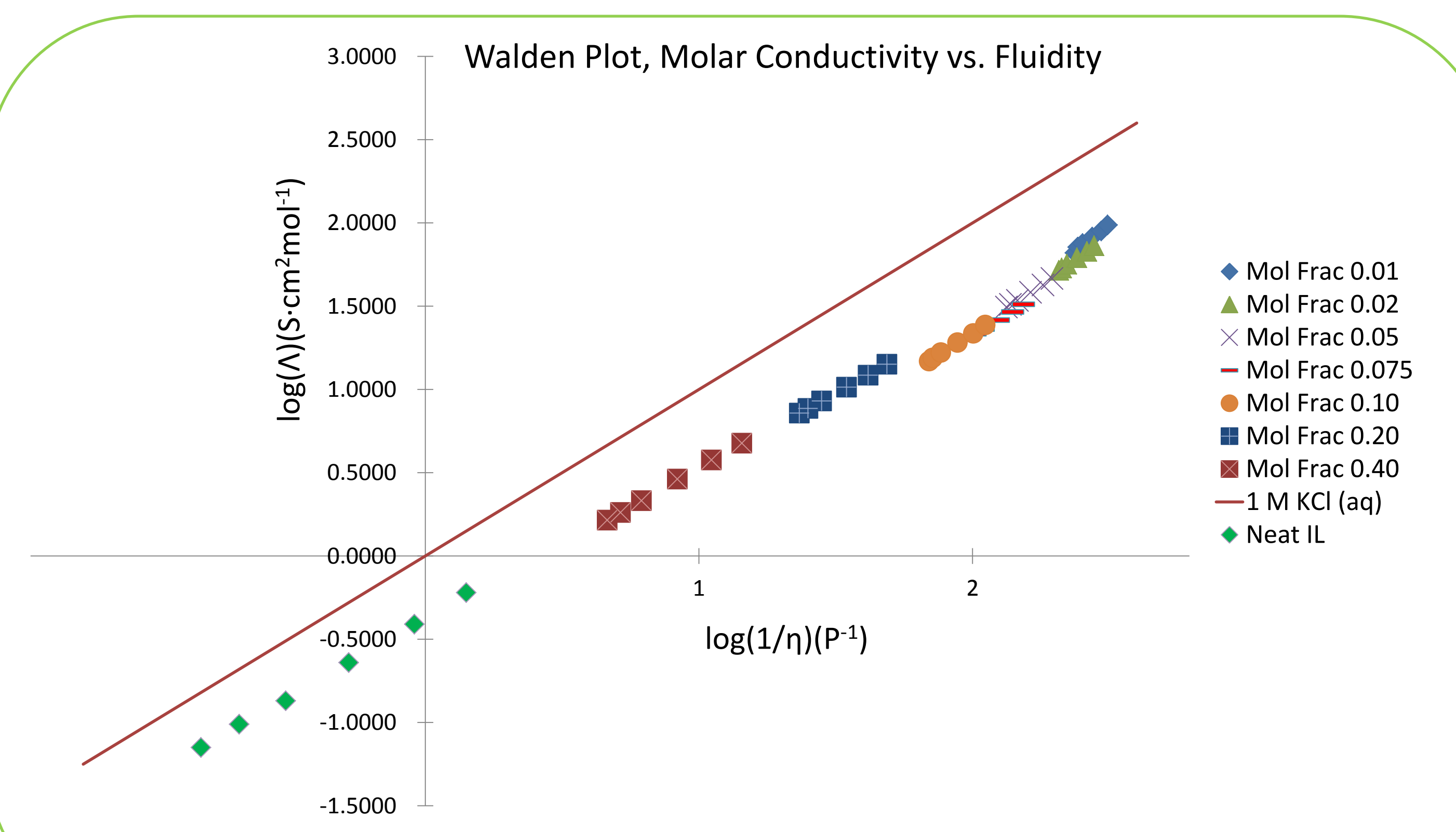


Figure 5. Logarithmic Walden plot of $[P_{2228}][4\text{-triaz}]$.

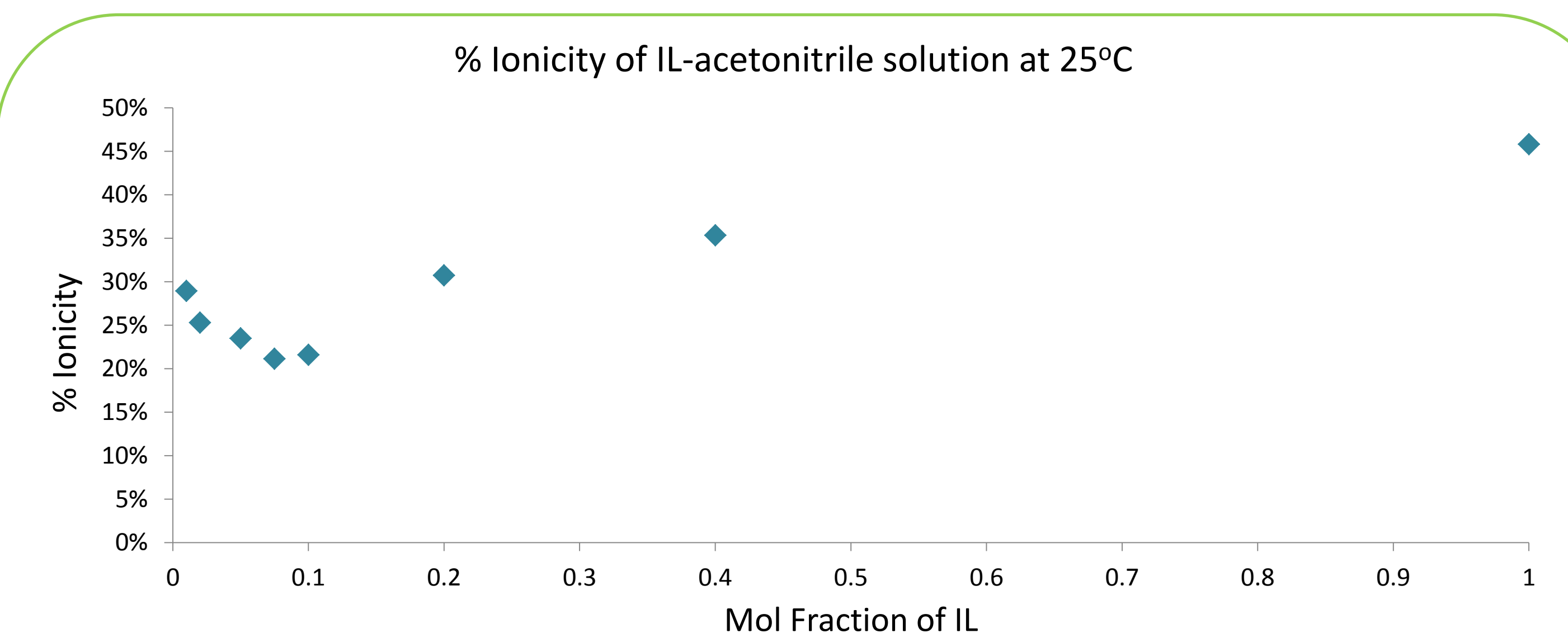


Figure 6. % ionicity of $[P_{2228}][4\text{-triaz}]$ derive from Walden plot. The minimum (21-22%) occurs around 0.01 mol frac. The maximum (46%) occurs in the neat IL.

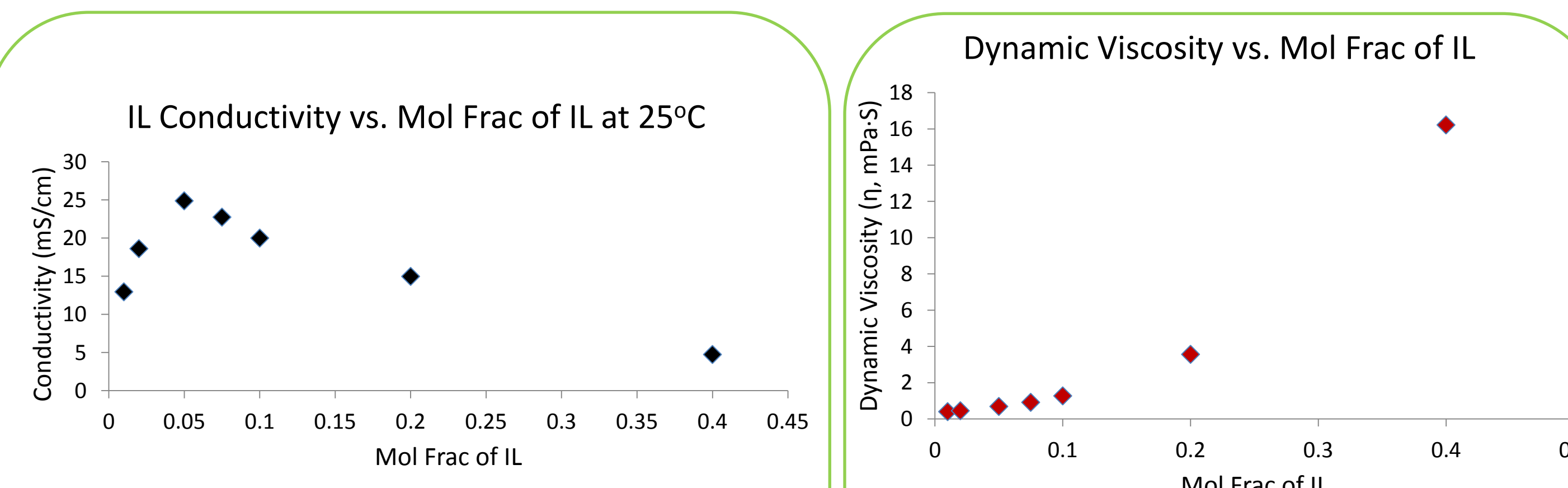


Figure 7. % ionicity of $[P_{2228}][4\text{-triaz}]$ derive from Walden plot. The minimum (21-22%) occurs around 0.01 mol frac.

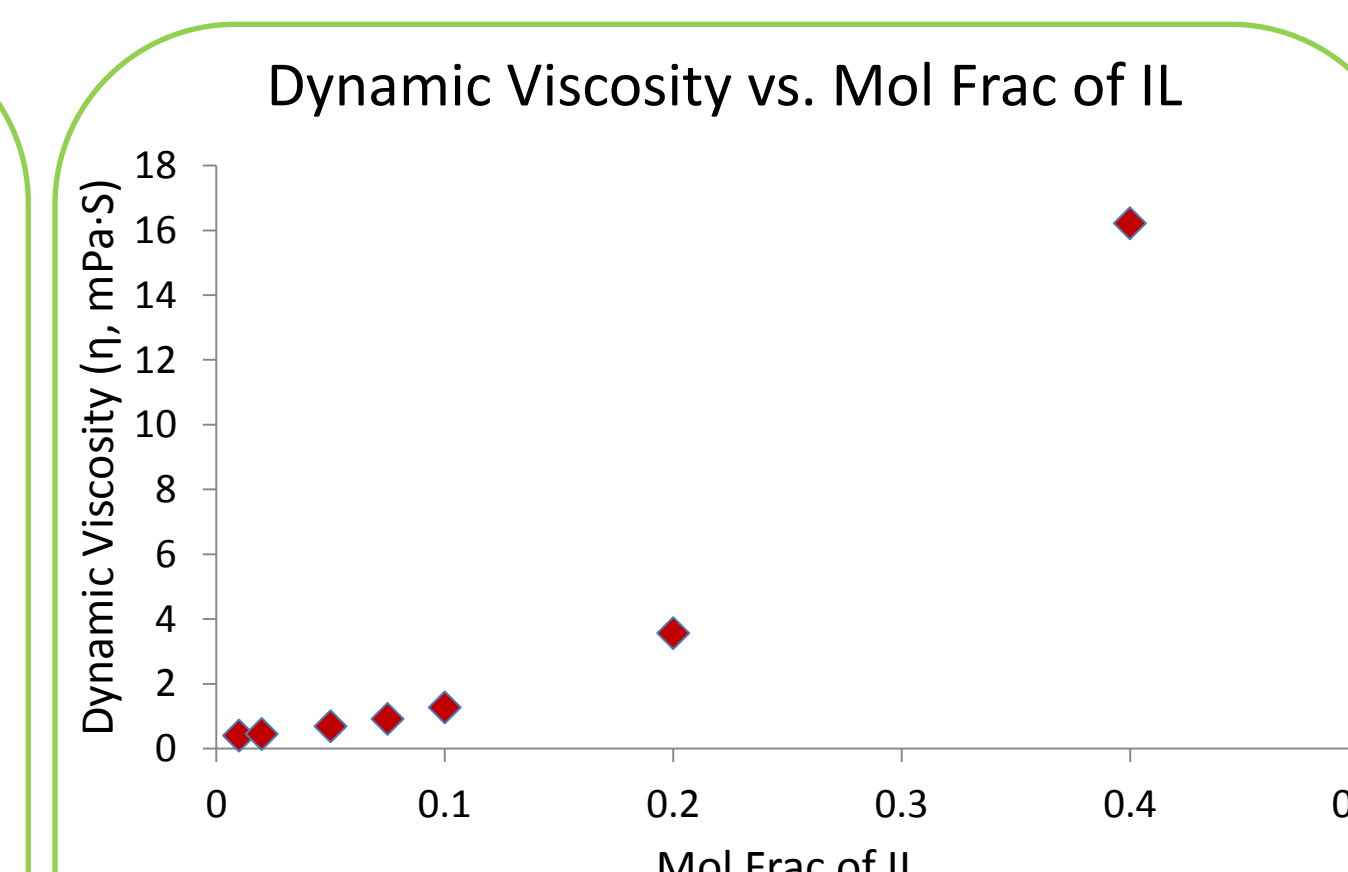


Figure 8. % ionicity of $[P_{2228}][4\text{-triaz}]$ derive from Walden plot. The minimum (21-22%) occurs around 0.01 mol frac.

Conclusion

As expected, the % ionicity started relatively high at lower mol fractions of IL. It reached a minimum (21-22%) around 0.10 mol fraction, before increasing nearly linearly to a maximum (46%) in the neat IL. Contrary to what was expected, solutions with larger % ionicities did not necessarily exhibit greater molar conductivities. The molar conductivity was dependent more on viscosity, suggesting viscosity determines molar conductivity more than the amount of ion dissociation. Acetonitrile seems to do little to reduce viscosity at higher mol fractions of $[P_{2228}][4\text{-triaz}]$ in IL-acetonitrile solutions. To improve the practical application of $[P_{2228}][4\text{-triaz}]$ as an agent for CO_2 capture, future research should be directed towards finding solvents that maintain low viscosities as mol fraction of IL increases, as this would maximize the anion availability and mobility.

Classroom Curriculum

Pedagogical Approach: Project-Based Learning

- Students learn content in the context of a real-world problem for which they are trying to devise a solution.
- The unique design of these units generates intrinsic motivation within students that often leads to better learning outcomes for both low- and high-performing students.⁴

Driving Question: Is it possible to make disposable batteries?

- Students will learn about the properties of electrolyte solutions in batteries and propose a design for a disposable battery.

Learning Objectives and Activities: Students will be able to...

- understand and model the solvation of an ionic compound and explain the role of polar solvents in dissolving ionic compounds.
- articulate the effect of intermolecular forces on the viscosity of an ionic solution.
- describe the effect of viscosity on the ability of an electrolyte solution to conduct electricity.
- build a noise-making device (see Figure 9) to qualitatively test the conductivity of a given solution.
- design experiments that analyze the effect of the molarity of an ionic solution on its conductivity/resistivity, use Excel to model the results of their experiments, and articulate conclusions of their experiments using written explanations.
- demonstrate an understanding of the pollutants in different types of batteries and devise and communicate alternative designs of batteries that would make them disposable/eco-friendly.

Assessments:

- Construction and successful implementation of conductivity tester
- Formal written lab report for designed experiments
- Presentation on the pollutants in batteries and explanation of alternative battery design

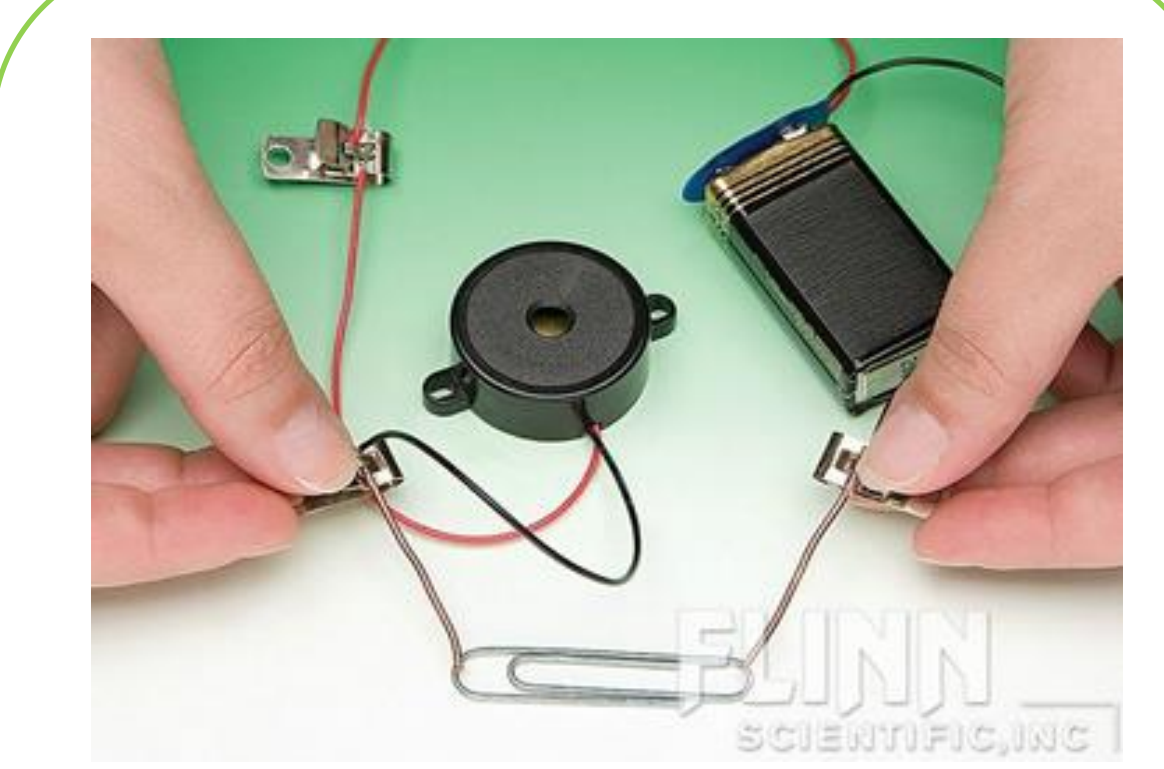


Figure 9. "Build Your Own Conductivity Tester—Student Laboratory Kit" sold by Flinn Scientific, Inc.

Acknowledgements

I would like to thank Liyuan Sun for advising me and working hard to prepare my samples all summer. I would also like to thank Thomas Gohndrone, Samuel Seo, Joseph Fillion, Dan Fagnant and Seungmin Oh for all of their help in navigating the lab. Finally, I want to thank Dr. Joan Brennecke for inviting me to join her research team and assisting me as I try to develop engaging and effective lesson plans for the high school classroom.



¹ S. Seo et al., *J. Phys. Chem. B*, 2014, **118**, 5740-5751.

² Data for neat IL (mol frac 1.0) from S. Seo, 2015, Dept. of Chemical and Biomolecular Engineering, University of Notre Dame, USA (unpublished).

³ S. Thawacker, N. D. Khupse and A. Kumar, *Phys. Chem. Chem. Phys.*, 2015, **17**, 475-482.