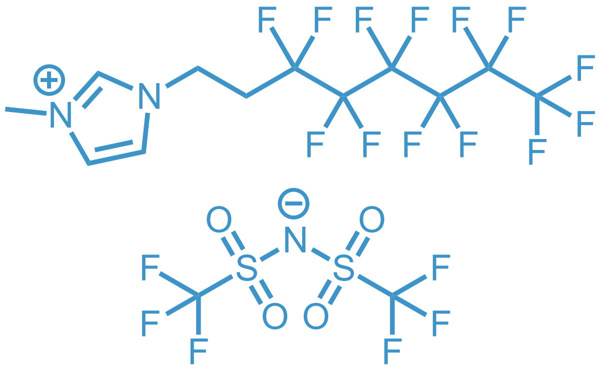
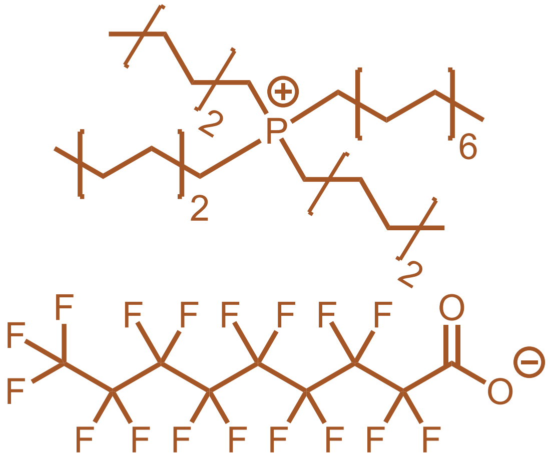
Understanding O_2 Absorption in Ionic Liquids





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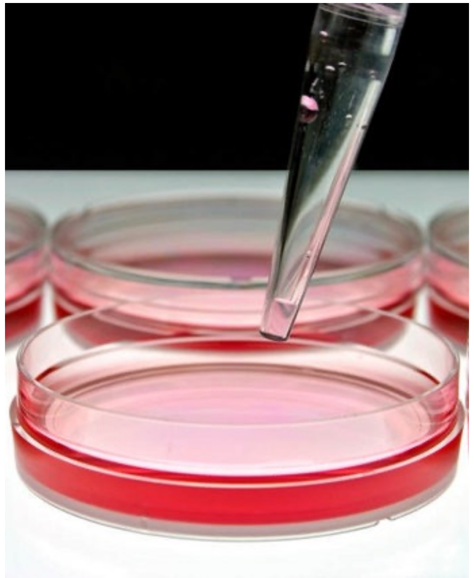
DOE CSGF Program Review

July 2021

Liquids with High O_2 Solubility Have Many Potential Uses



artificial blood
for trauma & surgery

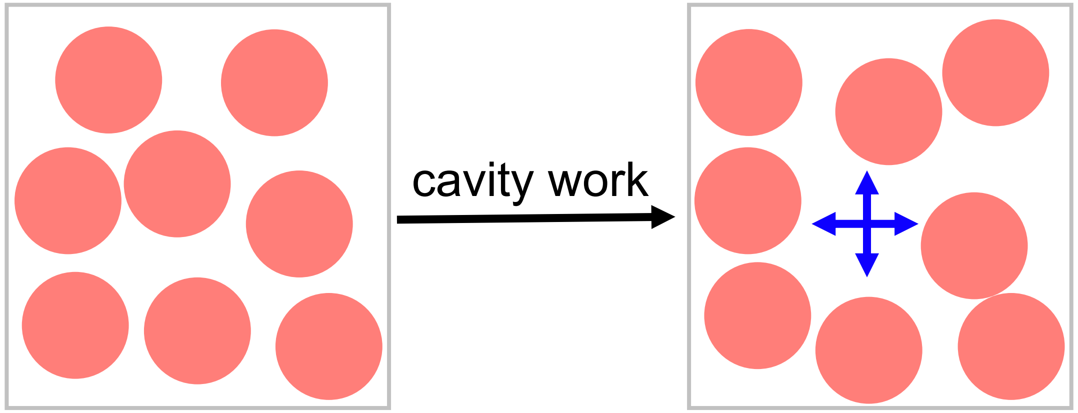


tissue engineering
& cell culture

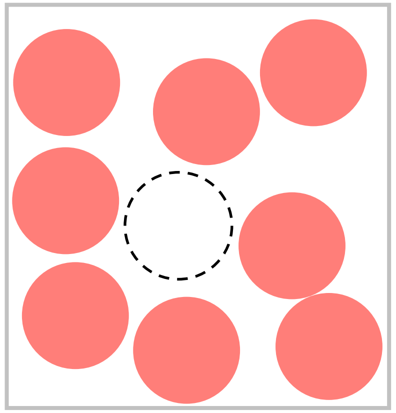
fuel cells
& electrocatalysts

How does Liquid Structure Explain Solubility Trends?

Liquid	O_2 Solubility at 25 °C and 1 bar (mmol/L)
water	1.3
n-hexane	15
n-perfluorohexane	28
bulk O_2	44



low cohesivity:
easy to form cavities



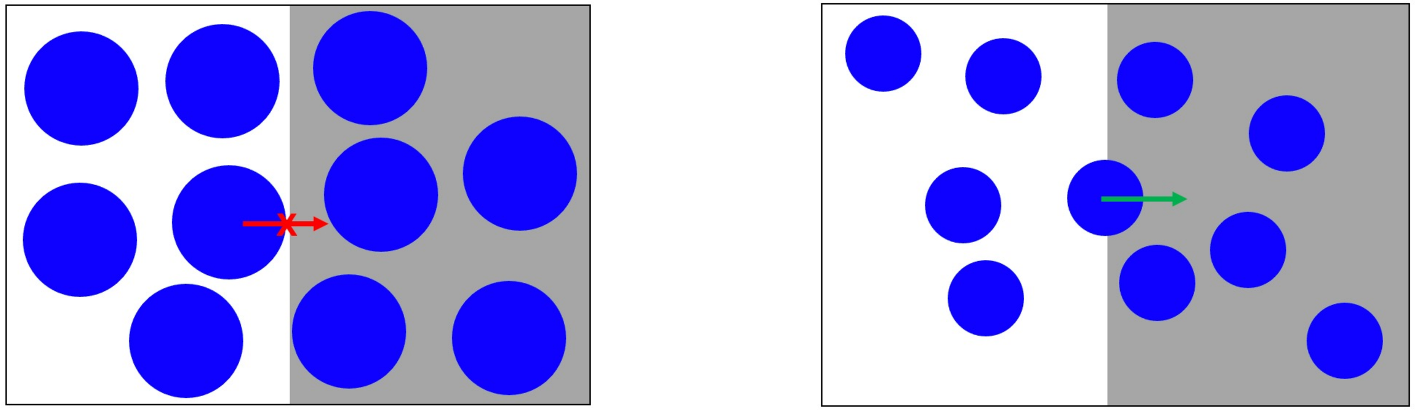
high free volume:
transient cavities are naturally large

Riess, *Artif. Cells, Blood Substitutes, Biotechnol.* **2005**, *33*, 47.; Clever, Battino, Miyamoto, Yampolski, Young, *J. Phys. Chem. Ref. Data* **2014**, *43*, 033102.

Compressibility Provides Information about Free Volume

Liquid	O_2 Solubility (mmol/L)	Isothermal Compressibility (10^{-10} Pa^{-1})
water	1.3	4.5
hexane	15	15
n-perfluorohexane	28	29

compressibility ≈ density fluctuations or variance in the average number of particles in a given volume

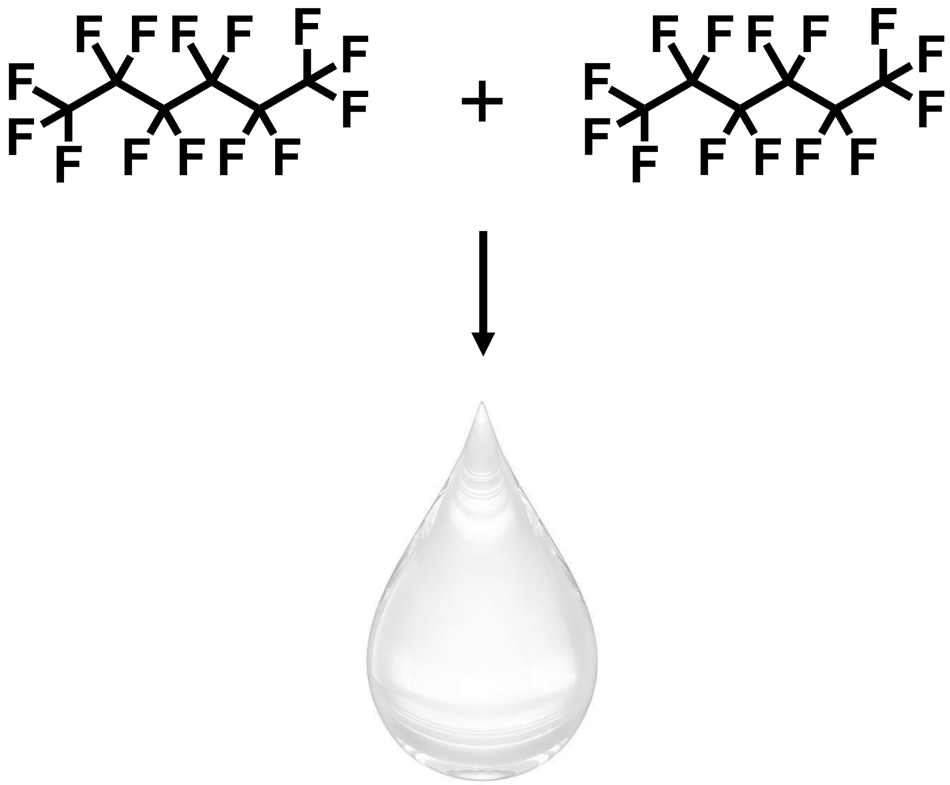


low compressibility high compressibility

Serratrice, Delpuech, Diguet, *Nouv. J. Chim.* **1982**, *6*, 489.
Riess, *Artif. Cells, Blood Substitutes, Biotechnol.* **2005**, *33*, 47.; Clever, Battino, Miyamoto, Yampolski, Young, *J. Phys. Chem. Ref. Data* **2014**, *43*, 033102.

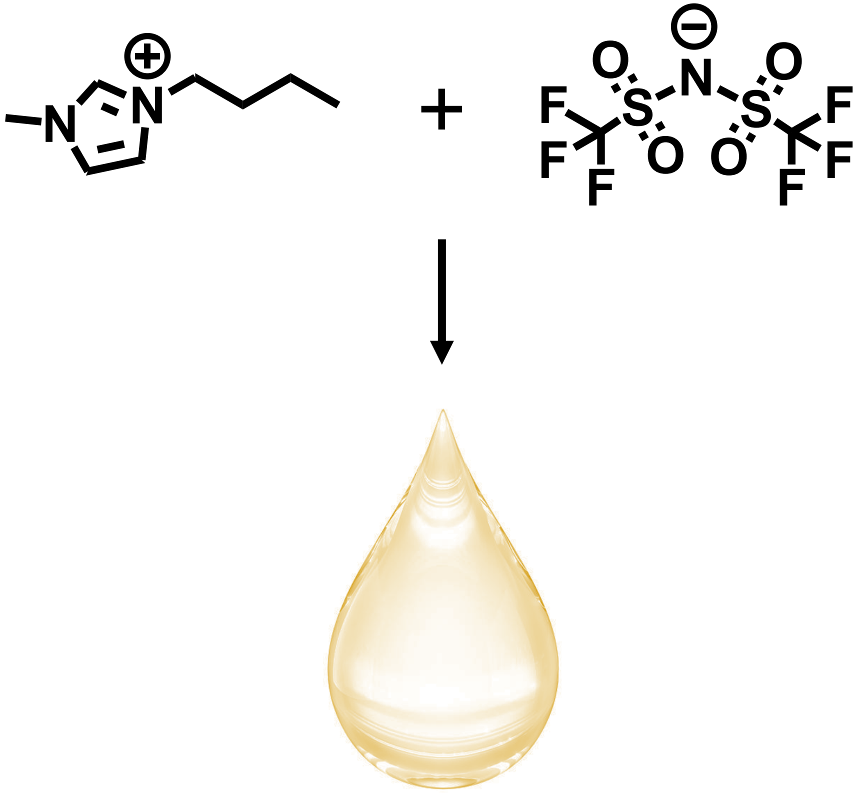
Manipulating Intermolecular Interactions in Liquids

Perfluorocarbons



liquids with high gas solubility

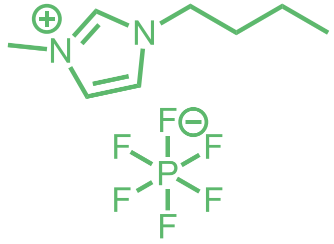
Ionic Liquids



low temperature molten salts
with negligible vapor pressure

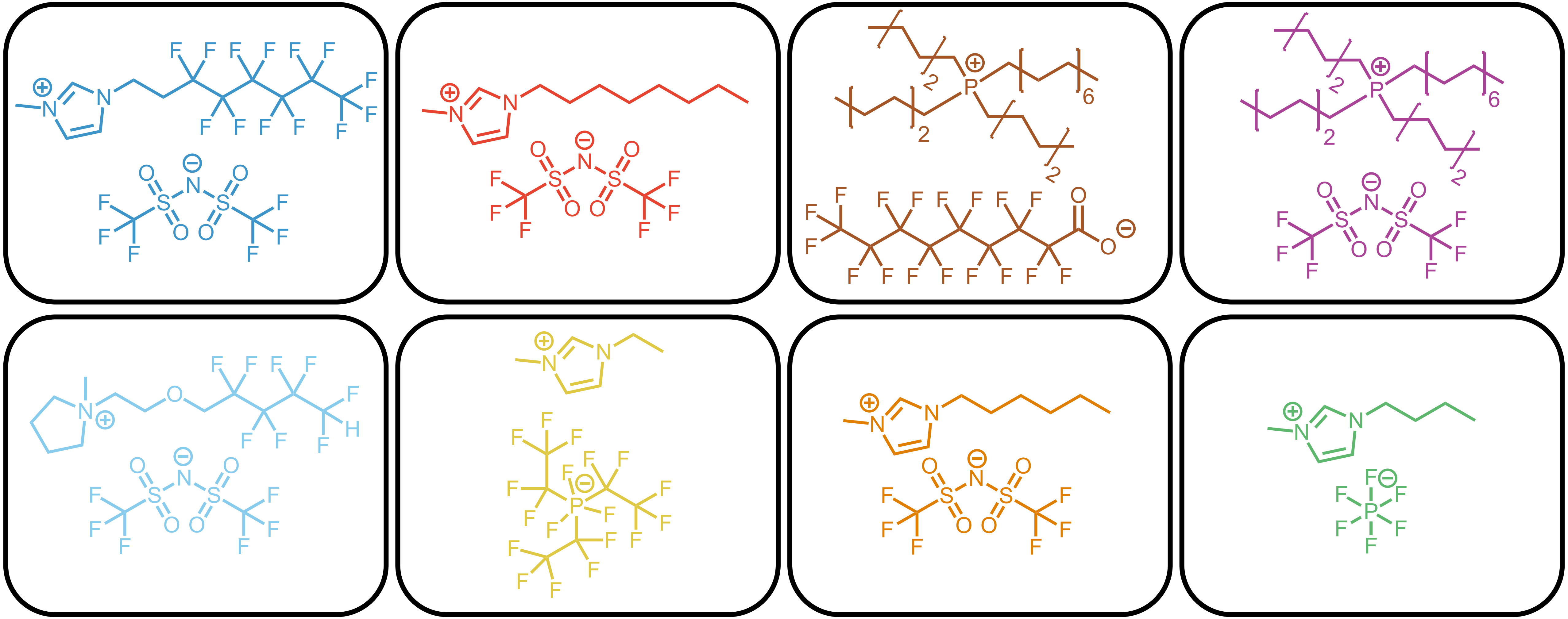
Riess, *Chem. Rev.* **2001**, *101*, 2797.; Welton, *Chem. Rev.* **1999**, *99*, 2071.

Ionic Liquids: Liquids with Low Oxygen Solubility and Compressibility

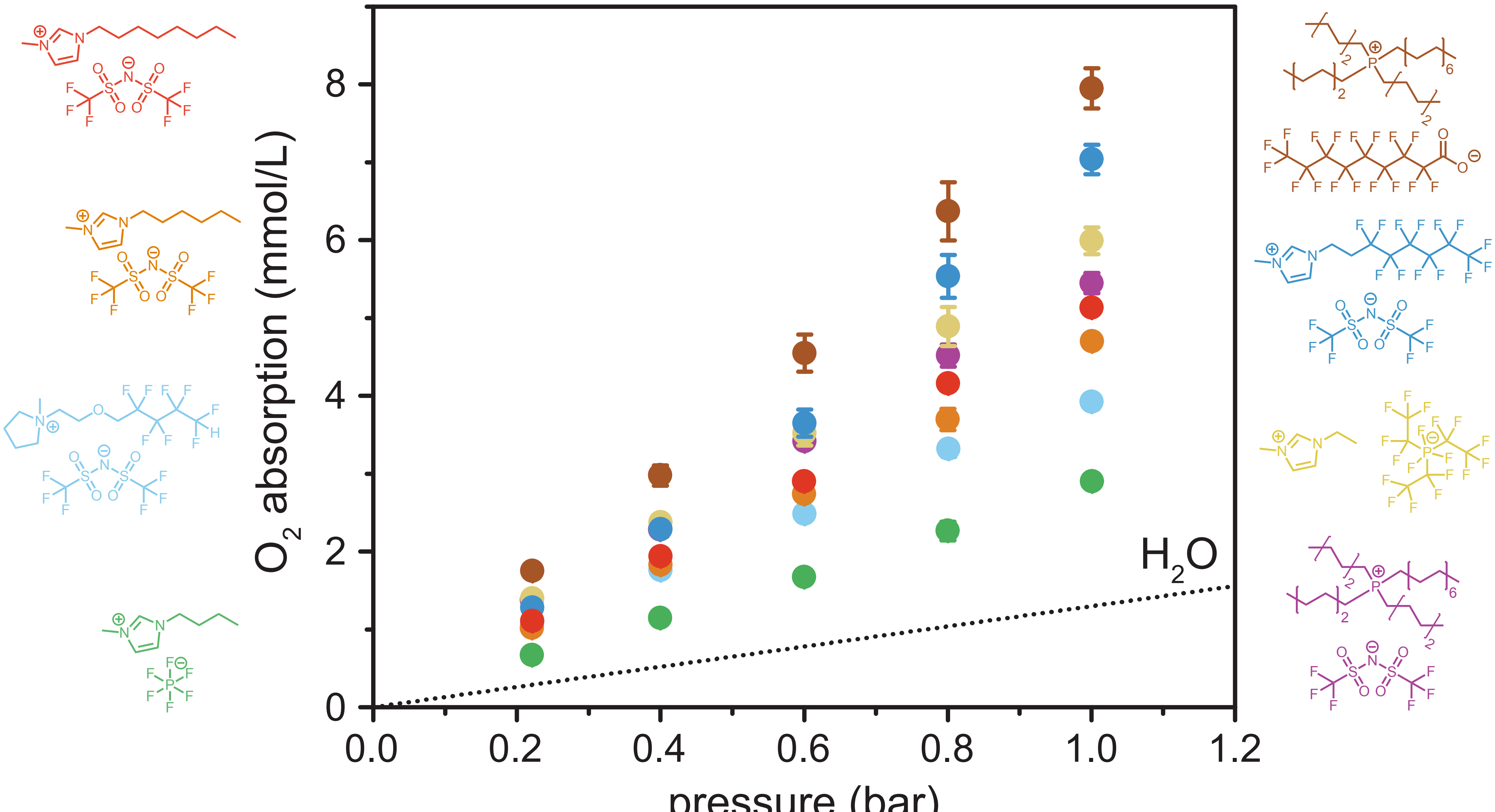
Liquid	O_2 Solubility (mmol/L)	Isothermal Compressibility (10^{-10} Pa^{-1})
water	1.3	4.5
	1.4	4.1
fluorinated ionic liquids	?	?
n-hexane	15	15
n-perfluorohexane	28	29

Anthony, Maginn, Brennecke, *J. Phys. Chem. B* **2002**, *106*, 7315.; Gu, Brennecke, *J. Chem. Eng. Data* **2002**, *47*, 339.;
Rumble, CRC Handbook of Chemistry and Physics, 99th Ed., CRC Press, Boca Raton, FL.; Serratrice, Delpuech, Diguet, *Nouv. J. Chim.* **1982**, *6*, 489.;
Clever, Battino, Miyamoto, Yampolski, Young, *J. Phys. Chem. Ref. Data* **2014**, *43*, 033102.

Developing a Library of Fluorinated Ionic Liquids

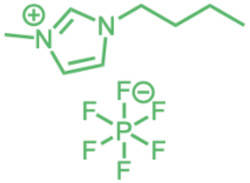
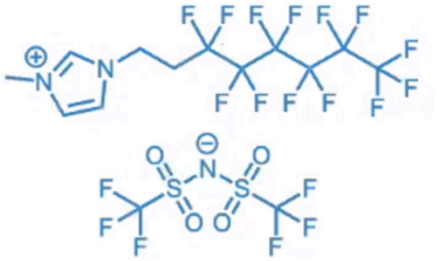


Fluorinated Ionic Liquids Display Higher O_2 Solubilities



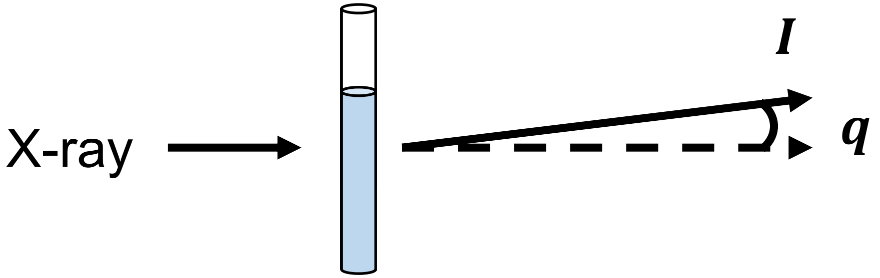
error bar is standard deviation of blank

Understanding Why Fluorination Increases O_2 Solubility

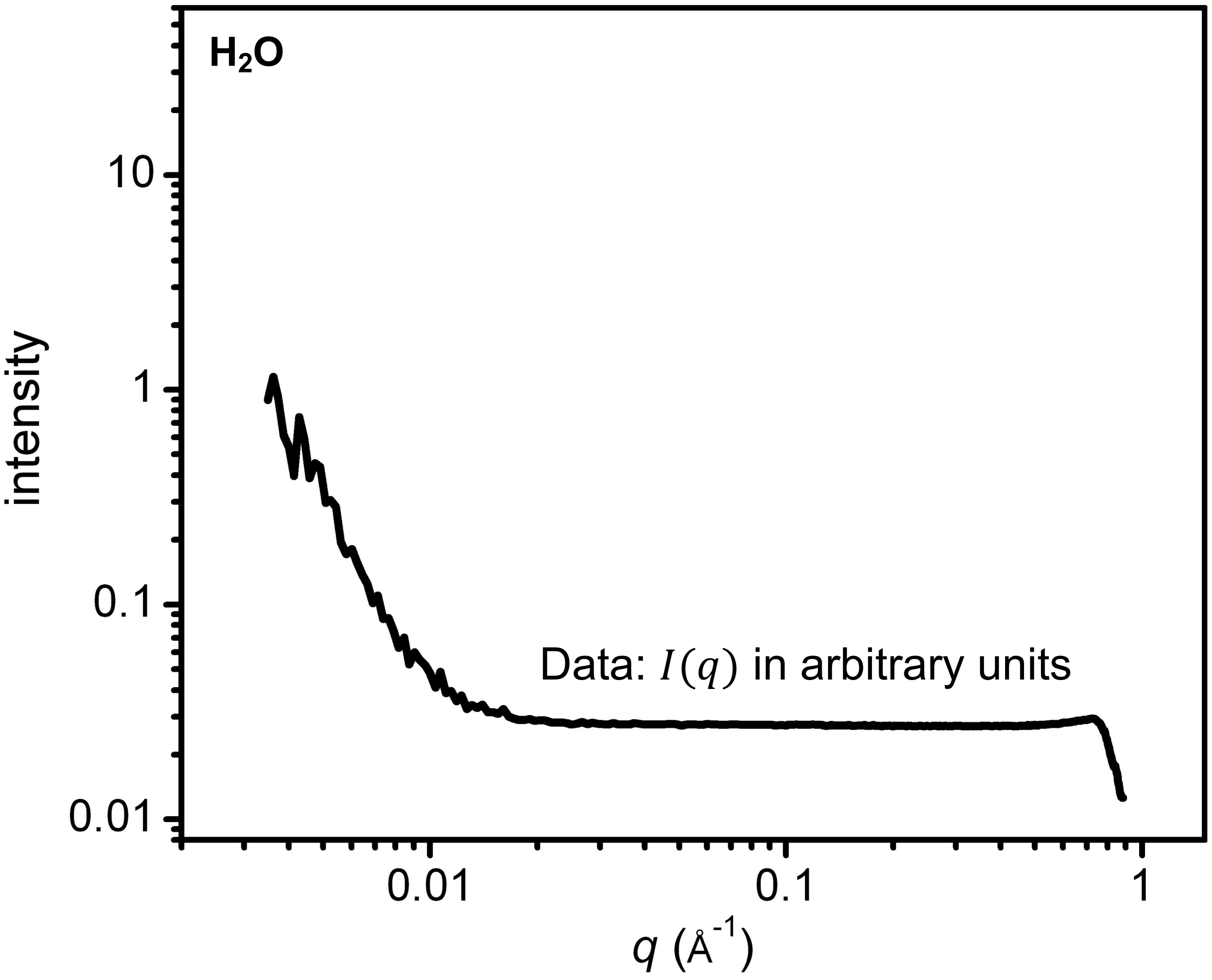
Liquid	O_2 Solubility (mmol/L)	Isothermal Compressibility (10^{-10} Pa^{-1})
water	1.3	4.5
	2.9	4.1
	7.9	**?**
n-hexane	15	15
n-perfluorohexane	28	29

Gu, Brennecke, *J. Chem. Eng. Data* **2002**, *47*, 339.;
Rumble, CRC Handbook of Chemistry and Physics, 99th Ed., CRC Press, Boca Raton, FL.; Serratrice, Delpuech, Diguet, *Nouv. J. Chim.* **1982**, *6*, 489.;
Clever, Battino, Miyamoto, Yampolski, Young, *J. Phys. Chem. Ref. Data* **2014**, *43*, 033102.

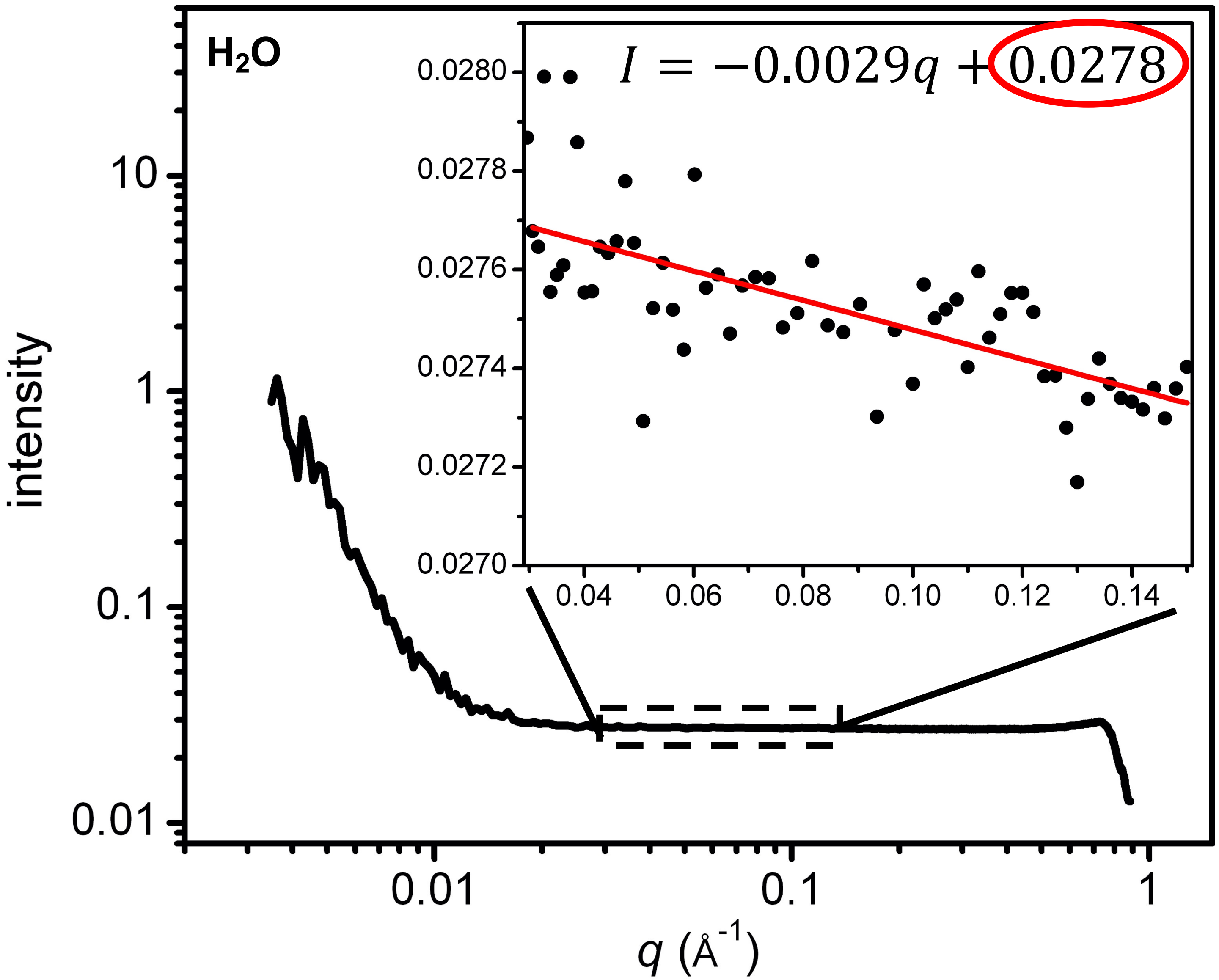
Extracting Isothermal Compressibility from SAXS Data



SAXS experiment



Extracting Isothermal Compressibility from SAXS Data



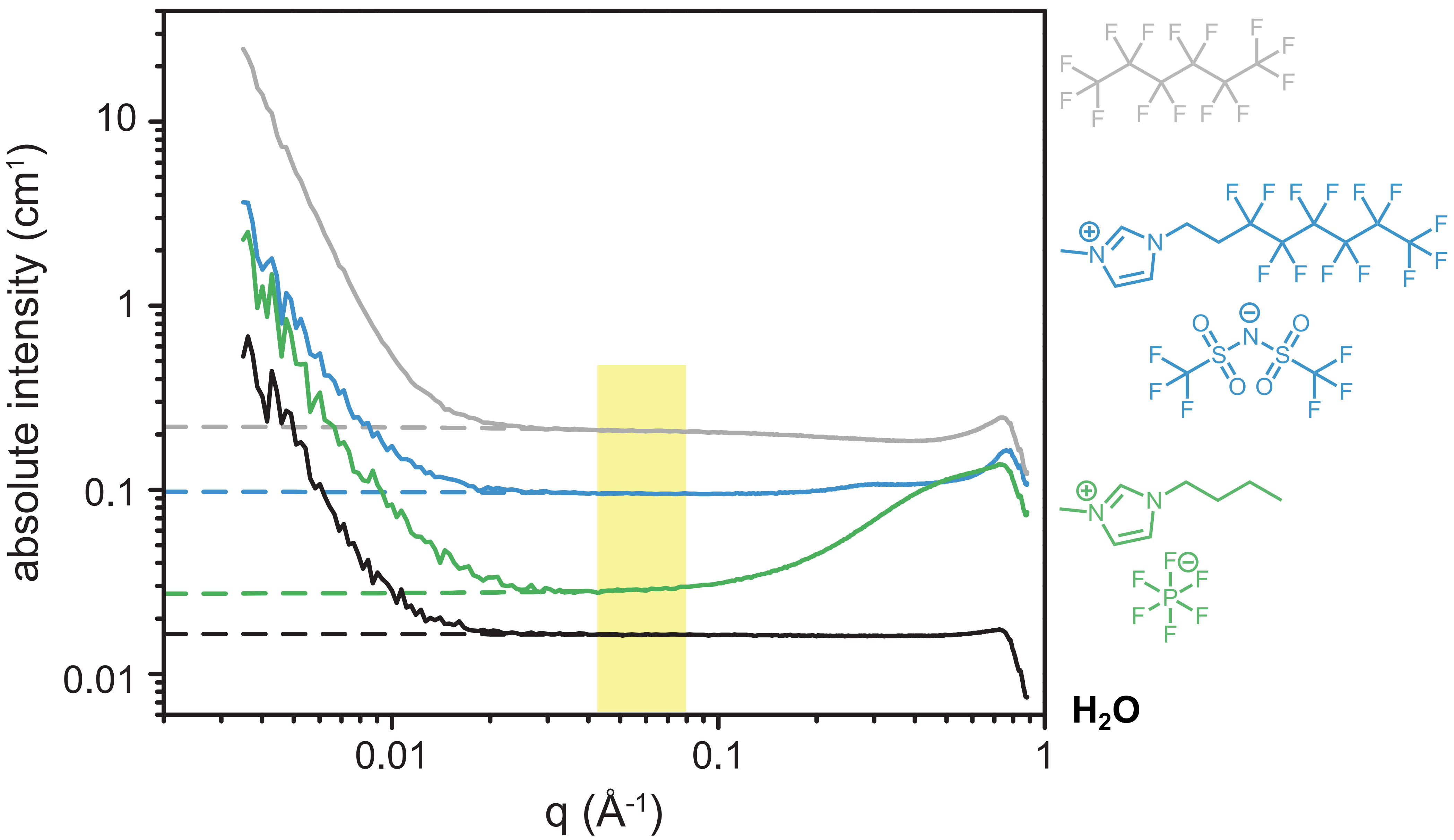
Using the SAXS intensity of H_2O at $q = 0$:

$$a = \frac{\boldsymbol{\beta_T} \rho^2 k_B T}{I(0)}$$

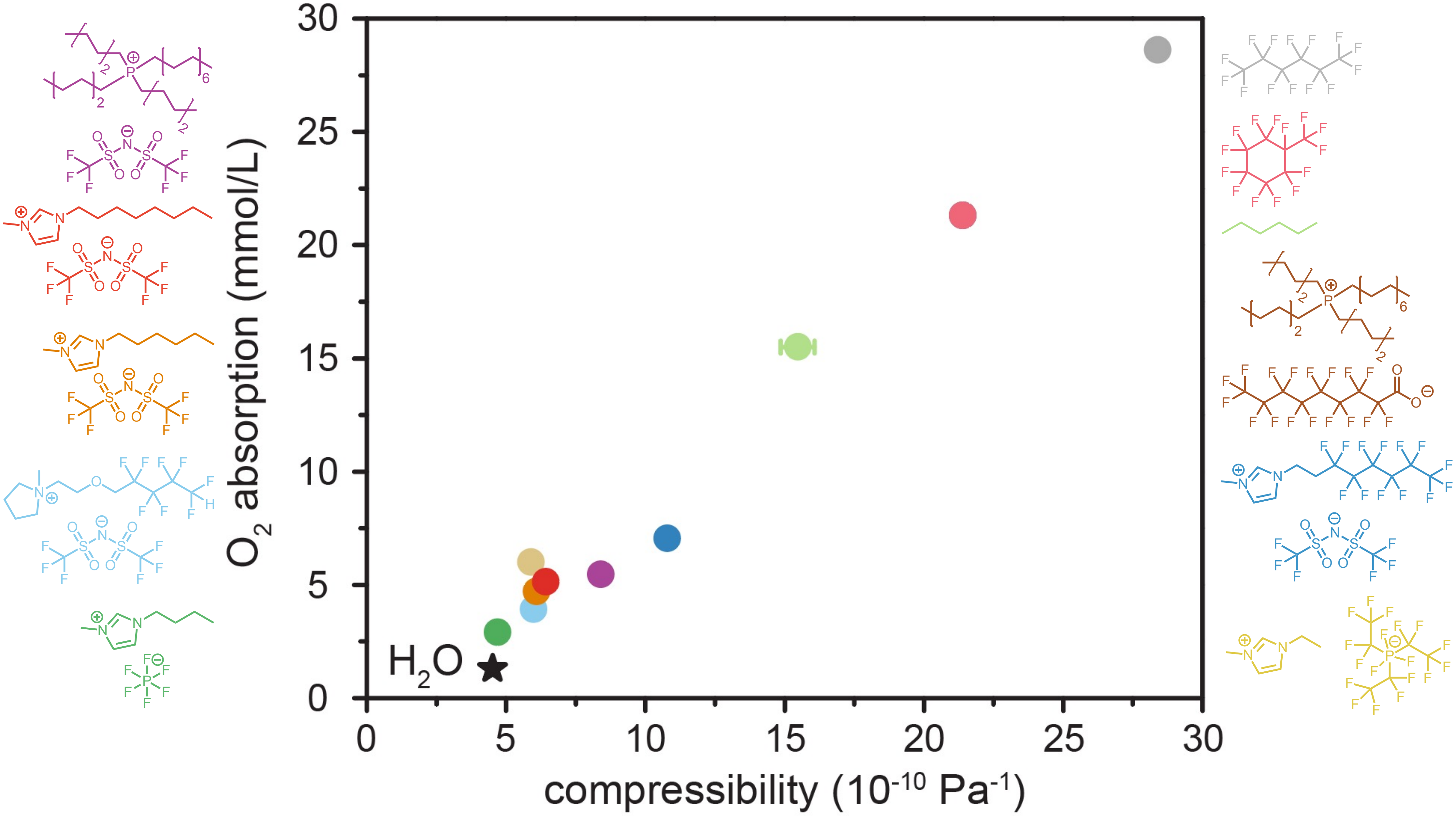
For all other samples, use the scaling factor determined from H_2O:

$$\boldsymbol{\beta_T} = \frac{a * I(0)}{\rho^2 k_B T}$$

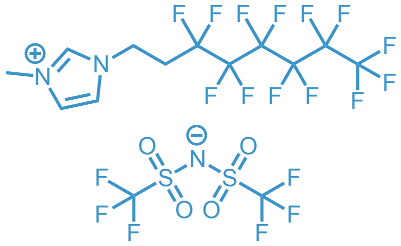
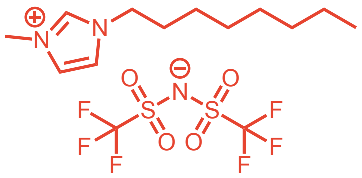
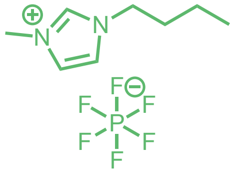
Compressibility Data: Visual Inspection

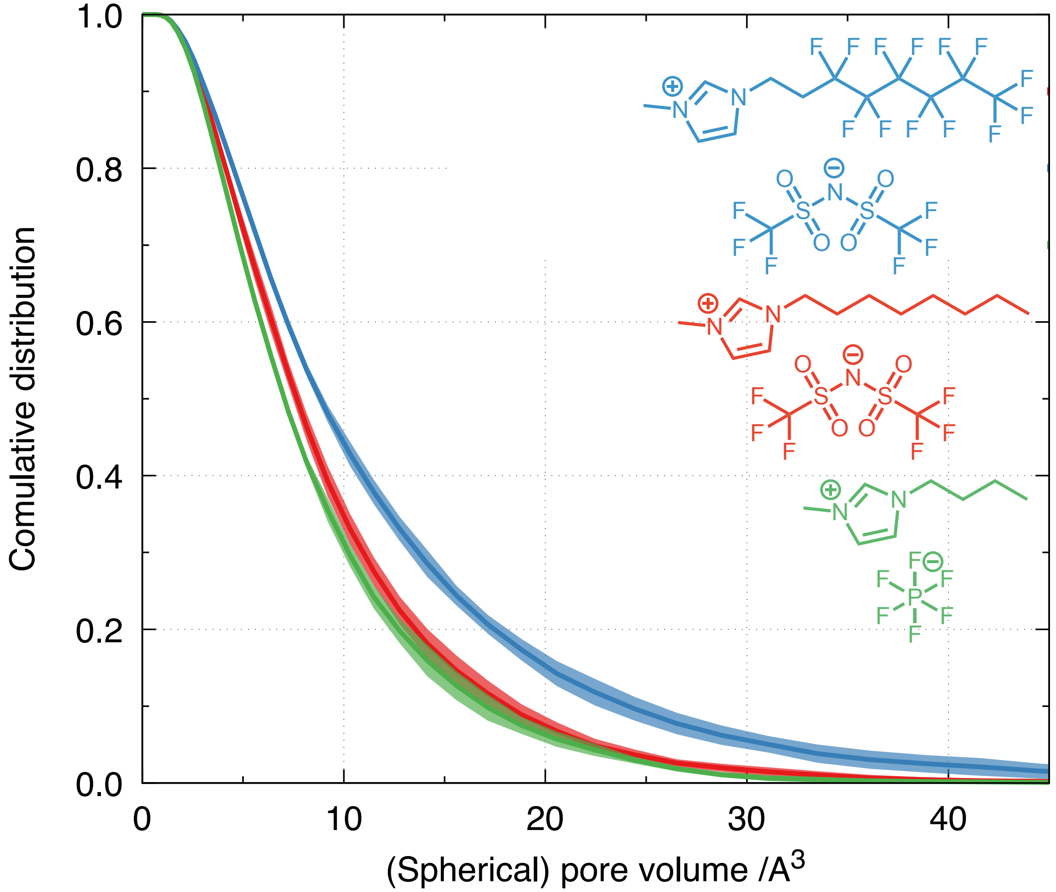


O_2 Solubility vs. Compressibility



Probing Free Volume *via* Molecular Dynamics Simulations

	Compressibility (10^{-10} Pa^{-1})	
Liquid	**Experimental**	**Simulated**
	10.8 ± 1	9.4 ± 0.15
	6.44 ± 1	7.8 ± 0.4
	4.7 ± 1	6.15 ± 0.15



Nicola Molinari

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