Investigating Dynamics in Novel Structured Electrolytes by NMR Relaxometry and Diffusometry

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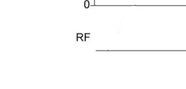
Background

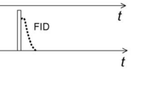
DES (Deep Eutectic Solvents): Glyceline is a deep eutectic mixture of **1:2 mole ratio** of **choline chloride (ChCl)** to **glycerol (GLY) (33mol%ChCl)**

Choline Chloride



Hydrogen bond acceptor

Glycerol

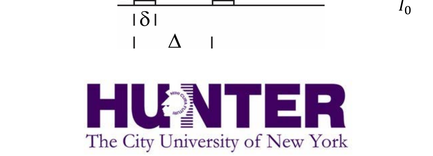


Hydrogen bond donor

Appeal for **electrochemical energy storage**

- Environmentally friendly
- Inexpensive and easy preparation
- Electrochemically stable
- High ionic conductivity

NOHMs (Nanoparticle Organic Hybrid Materials) are inorganic core to which polymeric chains ("canopy") are tethered ionically or covalently. "I" is used to indicate that the bond between the linker molecule and the polymeric canopy is ionic and "HPE" indicates that the constituent polymer is polyetheramine ("PE") with a high ("H") content of ether groups.

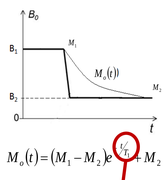


Electrochemical Applications

- Electrochemically stable
- Tunable Ionic conductivity
- Higher thermal-oxidative property
- Tunable viscosity

Approach

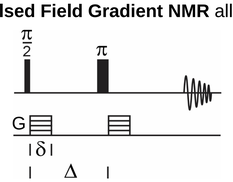
Fast Field Cycling NMR Relaxometry allows us to obtain information about the molecular dynamics of the electrolyte (dynamical processes from 10^{-9} to 10^{-3}s) by using an appropriate model.



$$M_0(t) = (M_1 - M_2)e^{-\frac{t}{T_1}} + M_2$$

Spin-lattice relaxation rate $R_1=1/T_1$

Pulsed Field Gradient NMR allows us to measure diffusion coefficients.



Stejskal-Tanner equation

$$\frac{I}{I_0} = \exp\left[-(G\gamma\delta)^2\left(\Delta - \frac{\delta}{3}\right)D\right]$$

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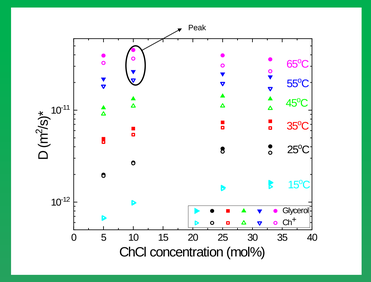
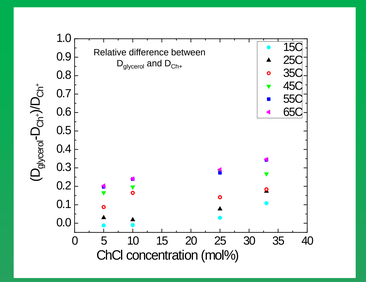
HIGHLIGHTS AND MAJOR FINDINGS

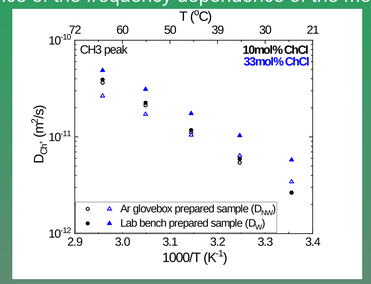
DES (Deep Eutectic Solvents)

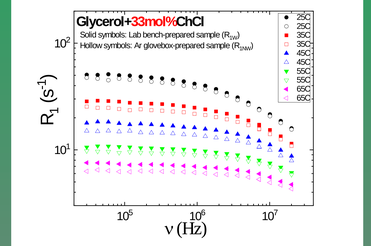
- Glycerol moves faster than Ch^+ does, at all ChCl concentrations and temperatures, in agreement with its lower molecular weight ($M_{wGly} < M_{wCh+}$).
- The partial disruption of glycerol network due to ChCl presence is evidenced by the fact that the relative difference between D_{gly} and D_{Ch+} in general increases with ChCl concentration at all temperatures.





- The presence of water in samples prepared in the lab bench makes the samples less viscous which is reflected by larger diffusion coefficients D^W (up to 85%). Interestingly, spin-lattice relaxation rates become larger (up to 25%), as a consequence of the frequency dependence of the measurements which are on the low-field side of the T_1 minimum.

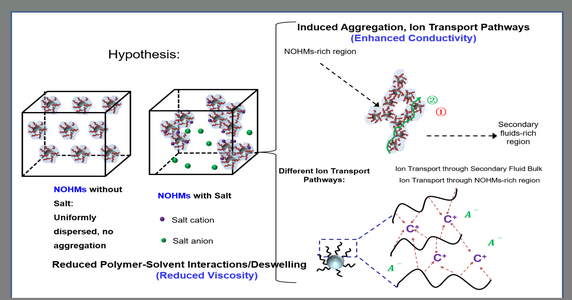


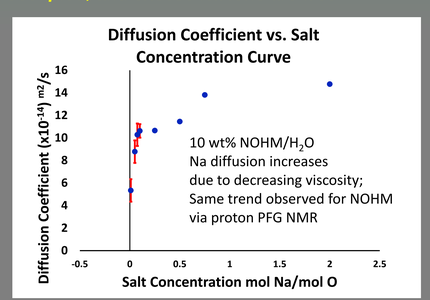


NOHM (Nanoparticle Organic Hybrid Materials)

- Though promising for many applications in electrochemistry, limited by high viscosities and low ionic conductivities
- Investigate reversibly tuning of the viscosity and transport properties of NOHMs-based electrolytes by doping salt

Hypothesis: NOHM diffusion increases in the presence of Na due to interactions with the polymer chains up to a 'Saturation Concentration' where all the ether sites are occupied, and excess Na ions are free





FUTURE DIRECTION

- A model to describe the relaxation profiles of DES, that will give us information about rotational and translational diffusion, is under consideration.
- The effect of water on diffusion coefficients will be test at even higher temperatures to confirm the crossover effect.
- In case of NOHMs, the diffusion coefficients of the NOHMs and water in this system also have been obtained by proton NMR and the results will be combined with the Na data shown here in order to verify or refine the hypothesis of ether chain–cation interaction.

Acknowledgements

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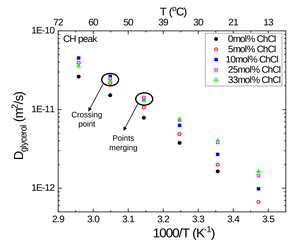
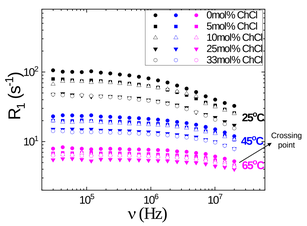
BEES Breakthrough Electrolytes for Energy Storage

Supporting data

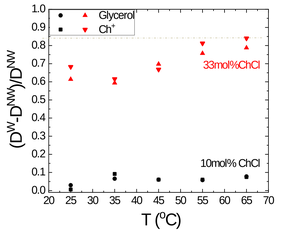
DES

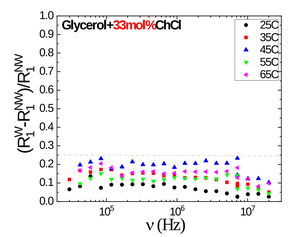
For T ≤ 45ºC, the diffusion coefficient *D* increases (R_1 decreases) with concentration of ChCl which is consistent with a decreasing viscosity. However, a **crossover effect** is observed at 55ºC (65ºC).





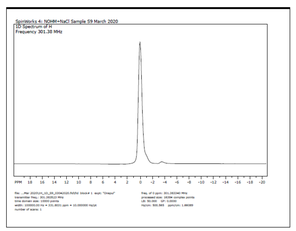
Water effect: relative difference between D^W ($R_1{}^W$) and D^{NW} ($R_1{}^{NW}$).

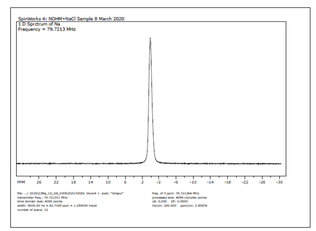




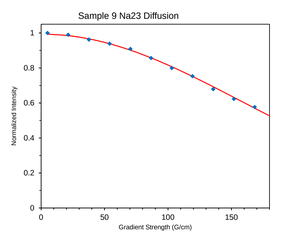
NOHM

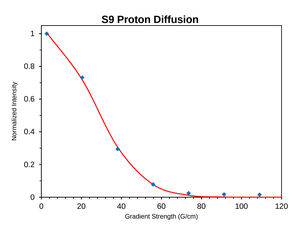
1D Spectrum of Proton and Na (Highest Concentration)





Diffusion Profile of Sodium and Proton





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