Physicochemical properties of some electrochemically relevant ions in protic ionic liquids

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❖ ELECTROCHEMICAL APPLICATIONS

ILs are actually the most promising solvents for electrochemical devices where more conventional media like water or organic solvents fail:

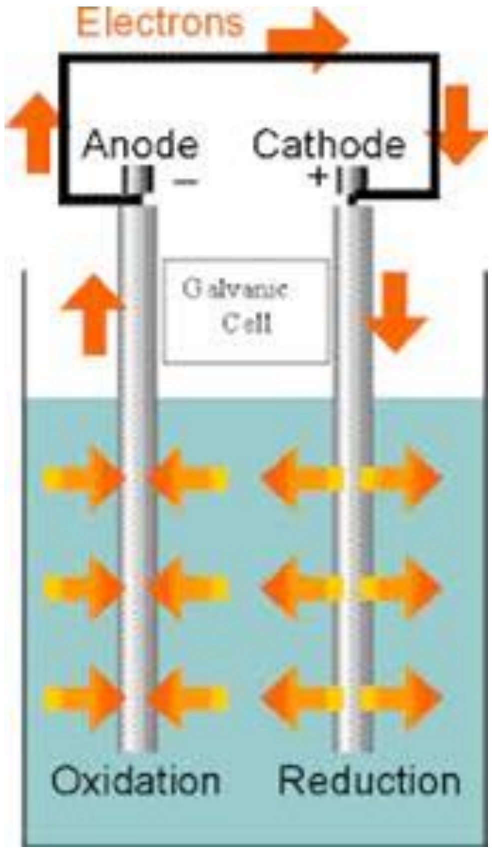
➢low vapour pressures => increases battery life by drying slower.

➢large conductivity values (1-10 mS cm^{-1})

➢large electrochemical windows of up to 6 volts

⇩

ILs are essentially electrochemically inert: MUST BE MIXED WITH SALTS



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❖ ELECTROCHEMICAL APPLICATIONS

	IL	density (g cm^{-3})	viscosity (mPa s)	conductivity (mS cm^{-1})
Aprotic Ionic Liquids (AIL)	$bmimBF_4$	1.26	99.2	3.5
	$bmimNTf_2$	1.43	52	4
	bmimSCN	1.07	51.7	4.2
	$emimBF_4$	1.28	37	14
	$emimNTf_2$	1.52	34	9.1
Protic Ionic Liquids (PIL)	**EAN**	1.22	**32**	**26.9**
	EAF	1.04	32	12.2
	BAF	0.97	70	3.1
	PeAF	0.95	78	1.5
	EOAF	1.14	66	6.2
	KCl 0.1 mol L^{-1}			12.88
	water	0.997	1	

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tunable solvents

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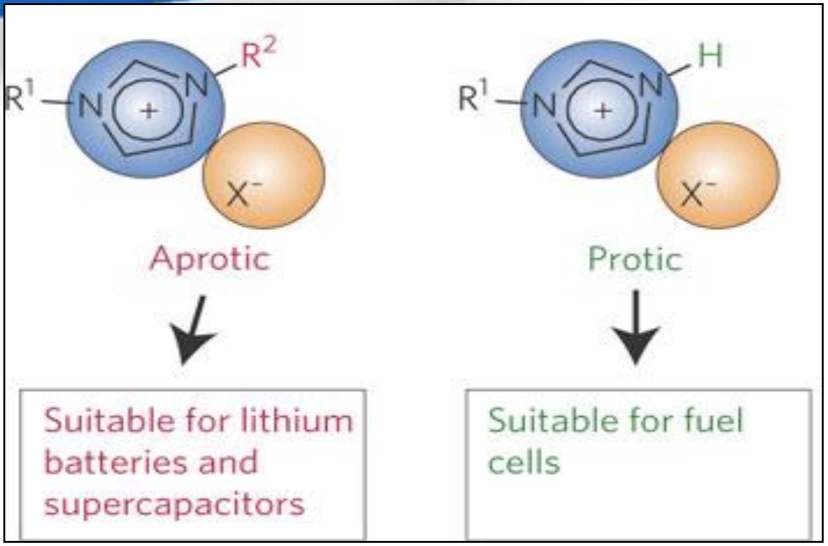
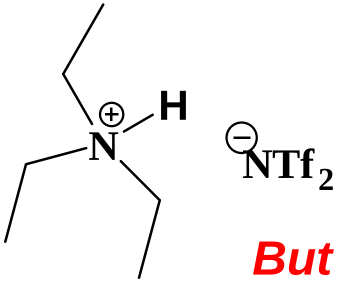
❖ ELECTROCHEMICAL APPLICATIONS

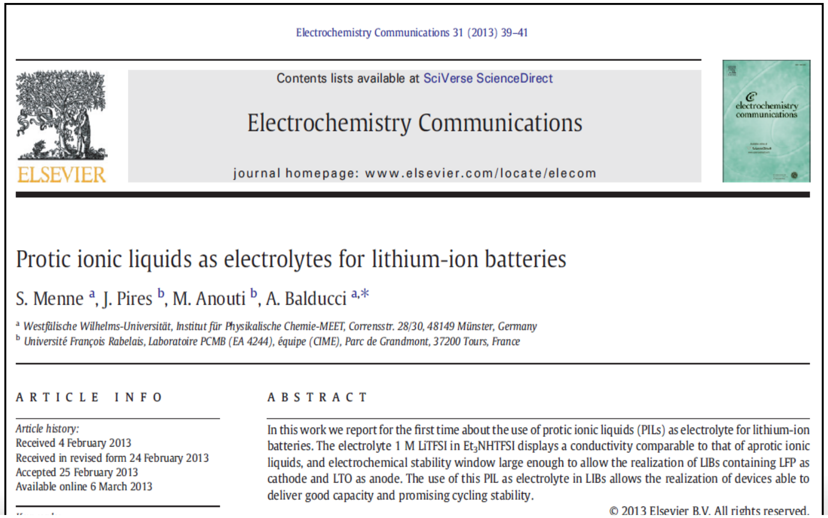
Each class of ILs traditionally considered suitable for a specific application.





But that is changing…

S. Menne et al., Electrochem. Comm. 31 (2013) 39



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Protic ionic liquids as electrolytes for lithium-ion batteries

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ABSTRACT

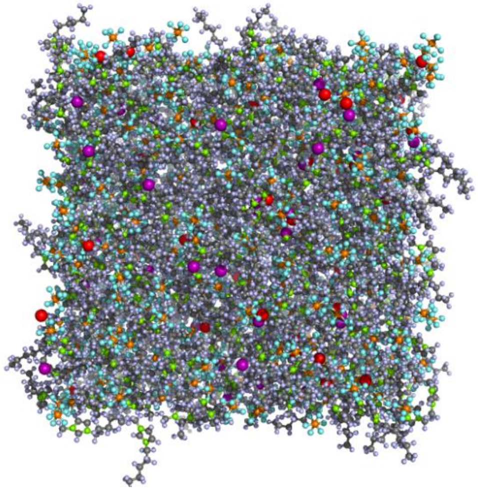
In this work we report for the first time about the use of protic ionic liquids (PILs) as electrolyte for lithium-ion batteries. The electrolyte 1 M LiTFSI in $Et_3NHTFSI$ displays a conductivity comparable to that of aprotic ionic liquids, and electrochemical stability window large enough to allow the realization of LIBs containing LFP as cathode and LTO as anode. The use of this PIL as electrolyte in LIBs allows the realization of devices able to deliver good capacity and promising cycling stability.

Solutions of electrochemically relevant salts in ILs must be considered

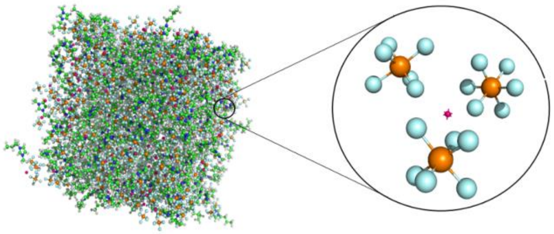
❖ SCOPE OF THIS WORK

Physical aspects of the solvation of ions in mixture with electrochemically relevant salts with ionic liquids.

- **Equilibrium and transport properties of mixtures of alkali, alkaline-earth and aluminum salts with protic ionic liquid:**
  - **- Density, sound velocity.**
  - **- Refractive index, surface tensions.**
  - **- Viscosity and electrical conductivity**



- **Which are the specific microscopic mechanisms of the nanostructured solvation of ions in the polar regions of PILs?**
  - **- MD results for coordination numbers, evolution of hydrogen bonds, cluster formation, diffusion coefficients, and velocity autocorrelation functions**



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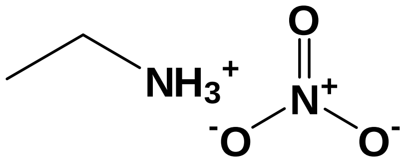
❖ RESULTS: Physicochemical properties

Ethylammonium nitrate



salts $LiNO_3$; $Ca(NO_3)_2$; $Mg(NO_3)_2$; $Al(NO_3)_3$

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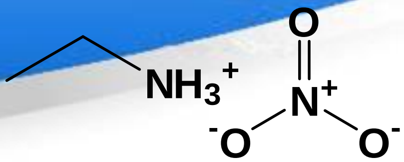
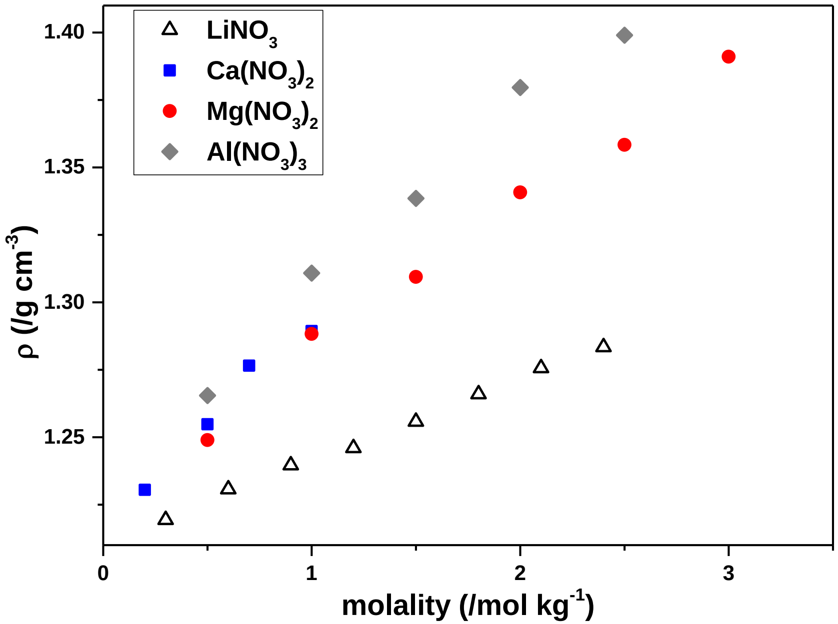
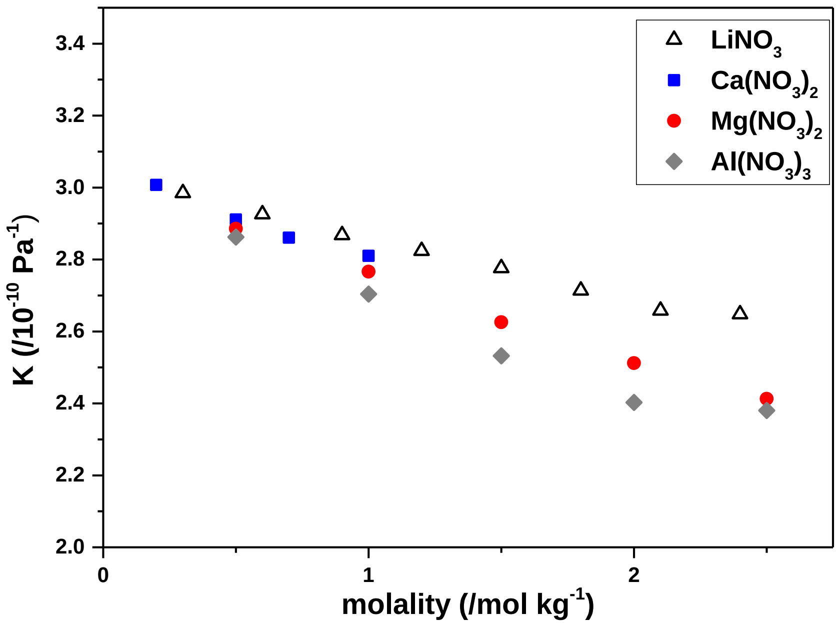
❖ RESULTS: Physicochemical properties



Volumetric properties of different salts at 298 K



Density



Adiabatic compressibility

$$K_S = \frac{1}{\rho v^2}$$

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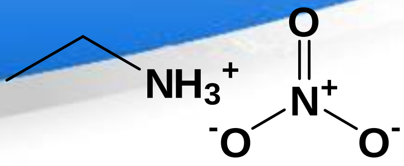
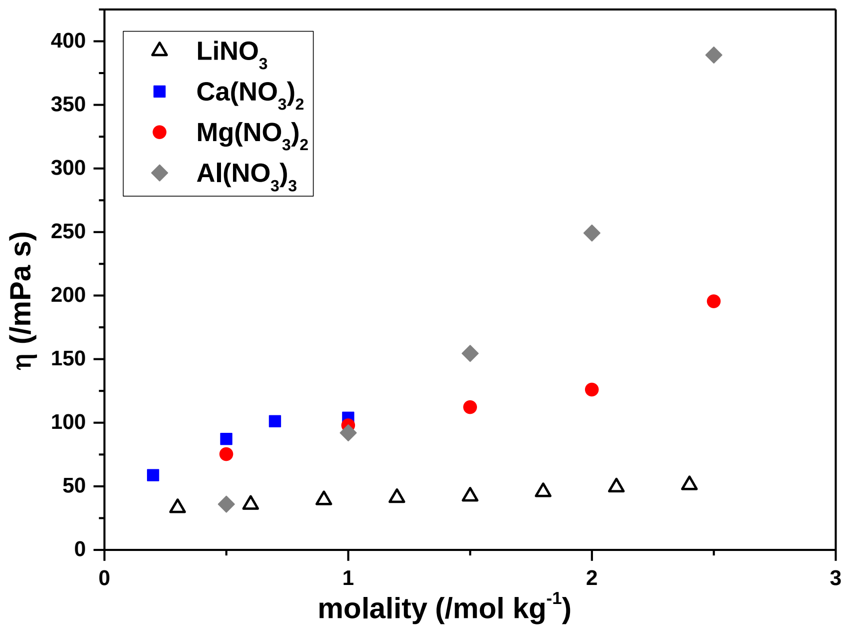
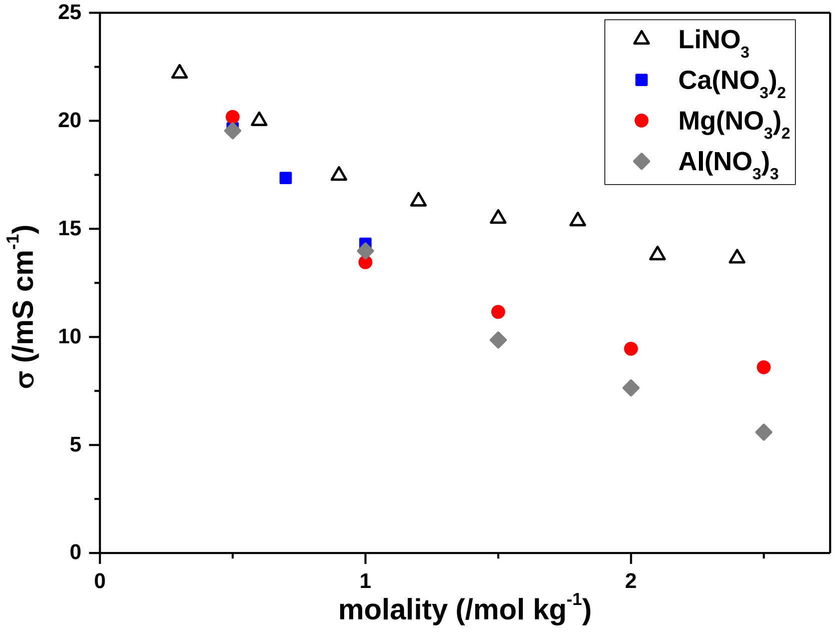
❖ RESULTS: Physicochemical properties



Other properties at 298 K



Viscosity



Electrical conductivity

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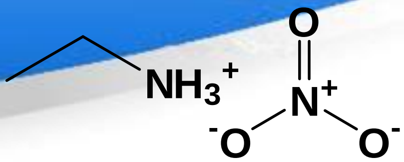
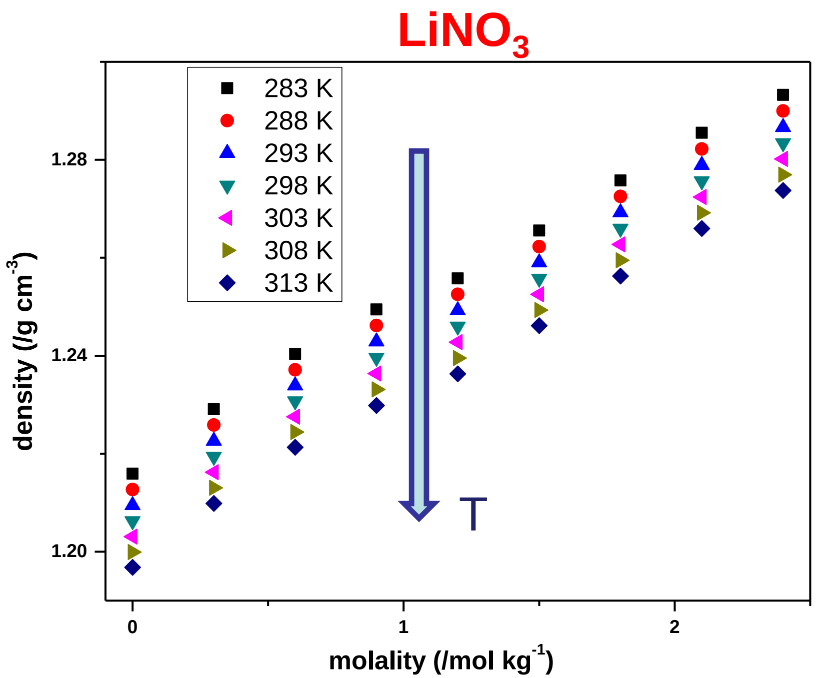
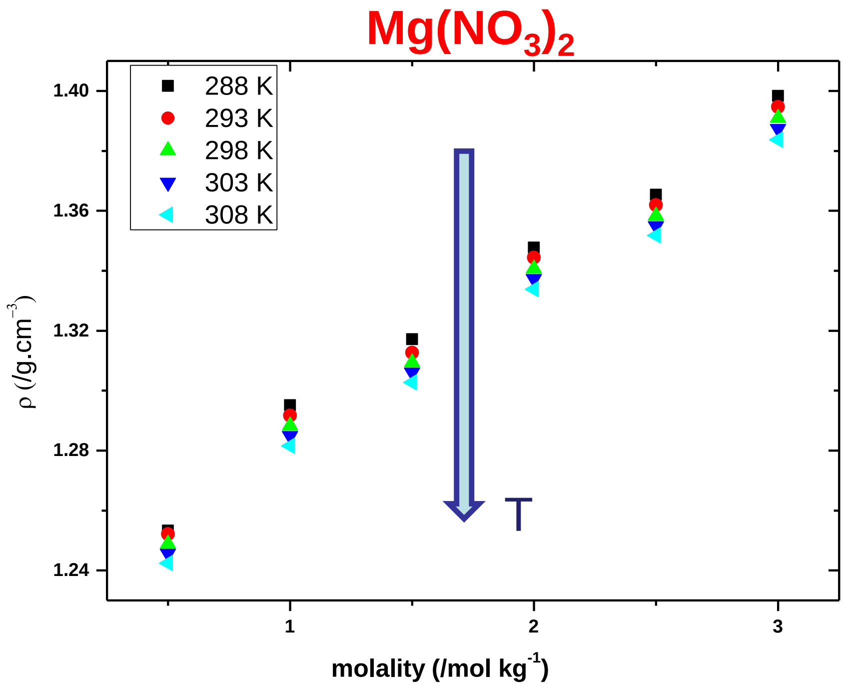
❖ RESULTS: Physicochemical properties



Effect of Temperature





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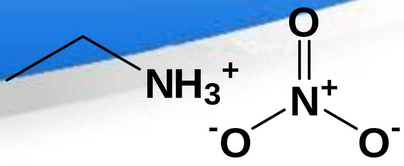
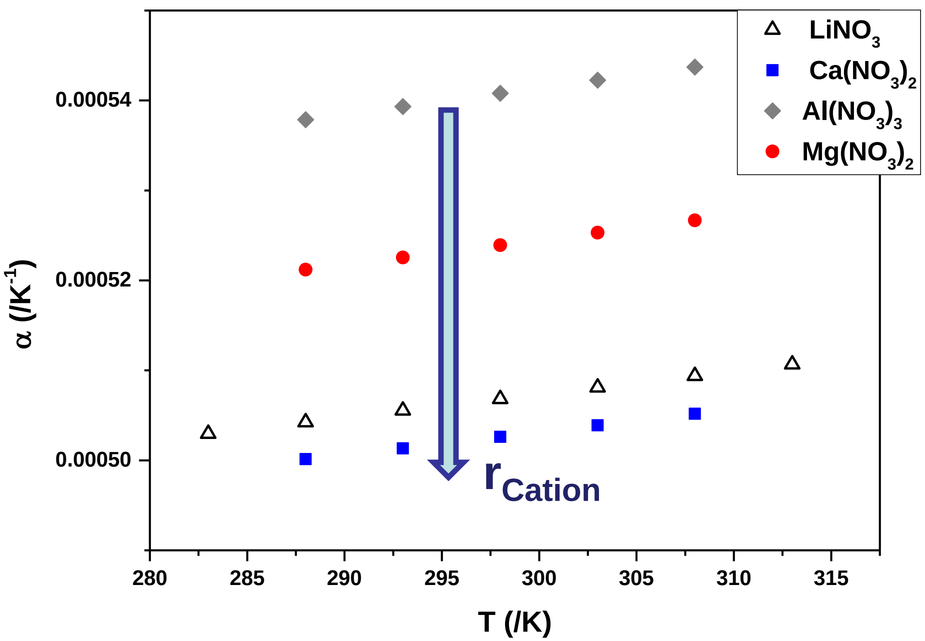
❖ RESULTS: Physicochemical properties



Thermal expansion coefficient

$$\alpha = -\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P$$



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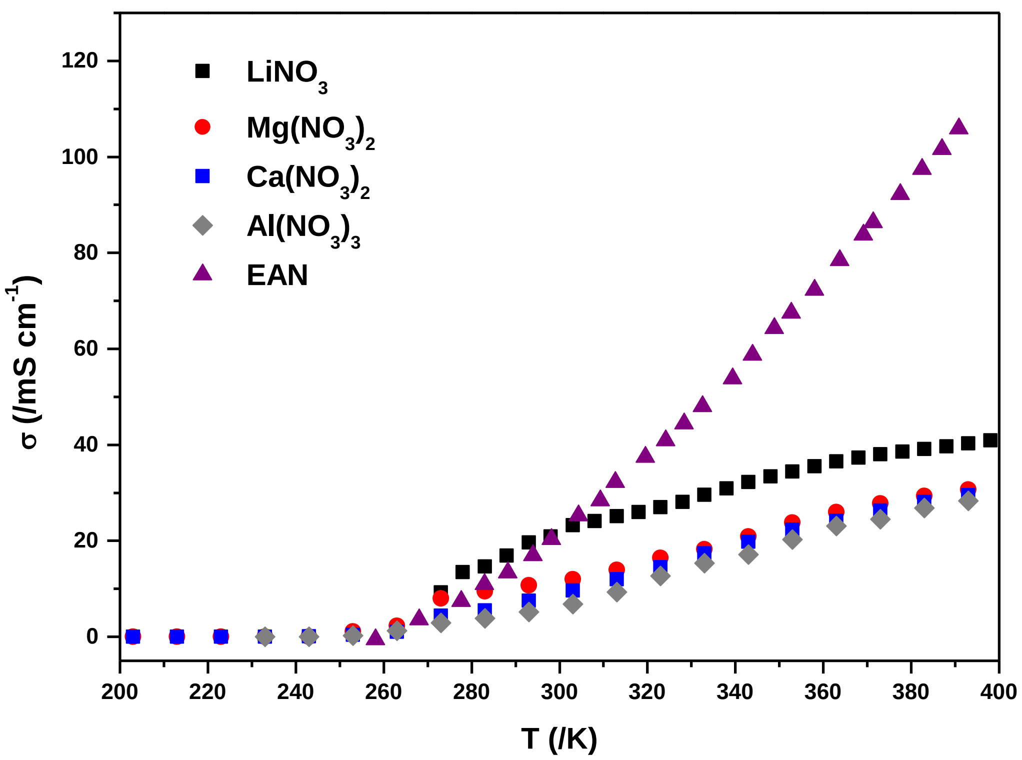
❖ RESULTS: Physicochemical properties

Electrical conductivity



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❖ Summary: preliminary results

We have observed that salt addition to EAN (generally) induces:

- **density, sound velocity and viscosity increments**
- **conductivity and compressibility decrements**

Increasing valence produces less compressible mixtures.

Which type of ion solvation explains this observations?

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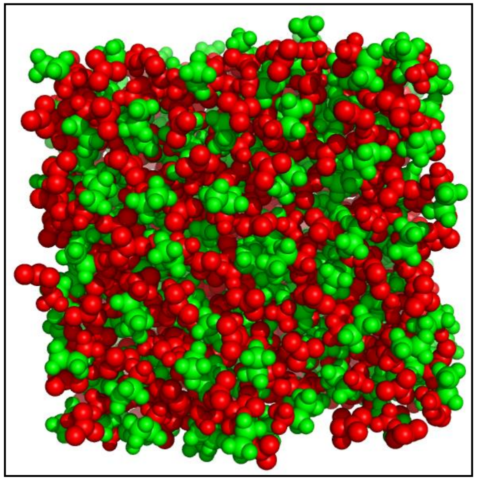
❖ RESULTS: radial distribution functions (RDFs).

- Electrostatic + vdW interactions

+

- Strong network of hydrogen bonds in PILS.

Formation of polar (anion and cation polar group) and apolar domains (methylene and methyl groups) in the bulk.



Polar and apolar domains in pure EAN.

How does C^+ accommodate into the two networks?
Why salts precipitate?

…. By a Molecular Dynamics study

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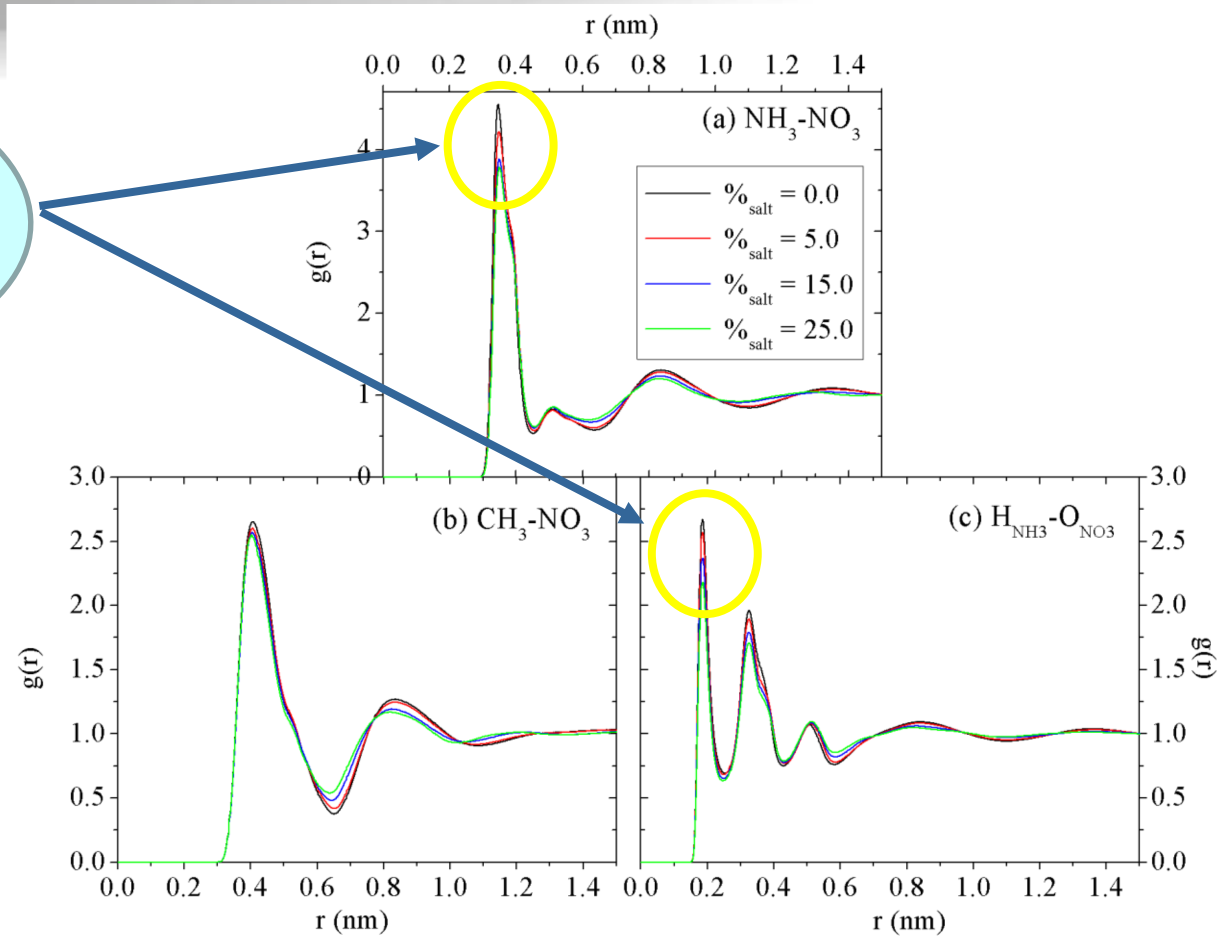
❖ RESULTS: radial distribution functions (RDFs).

Li is included in the polar domain of the IL and gradually destroys the network of H-bonds

Structure of ILs: only slightly affected by salt addition



T. Méndez-Morales et al. JPCB, J. Phys. Chem. B 2014, 118, 761−770

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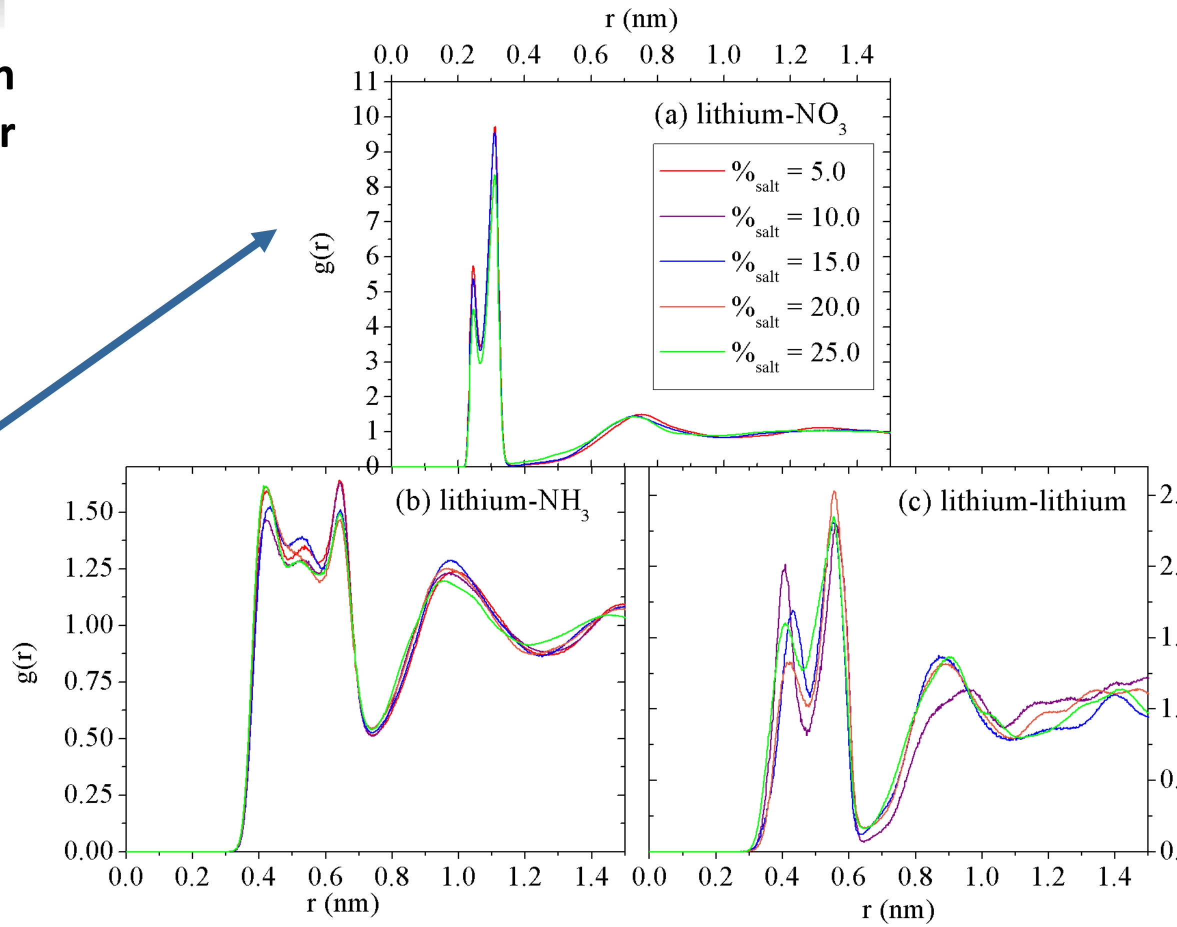
❖ RESULTS: radial distribution functions (RDFs).

How is the salt cation placed in the polar nanoregions?



Stronger coordination of Li with NO_3^-.

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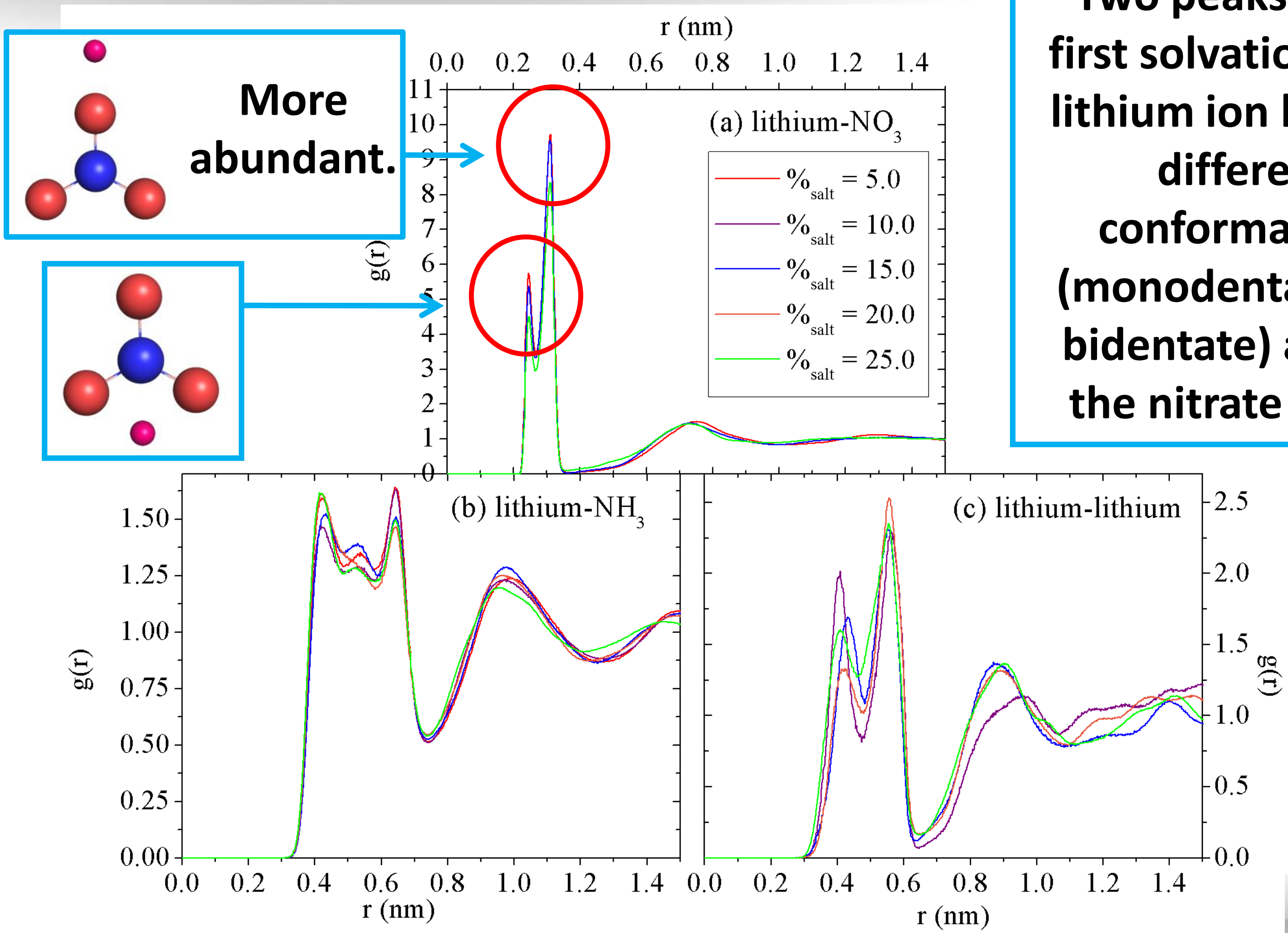
❖ RESULTS: radial distribution functions (RDFs).



Two peaks in the first solvation shell: lithium ion has two different conformations (monodentate and bidentate) around the nitrate anion.

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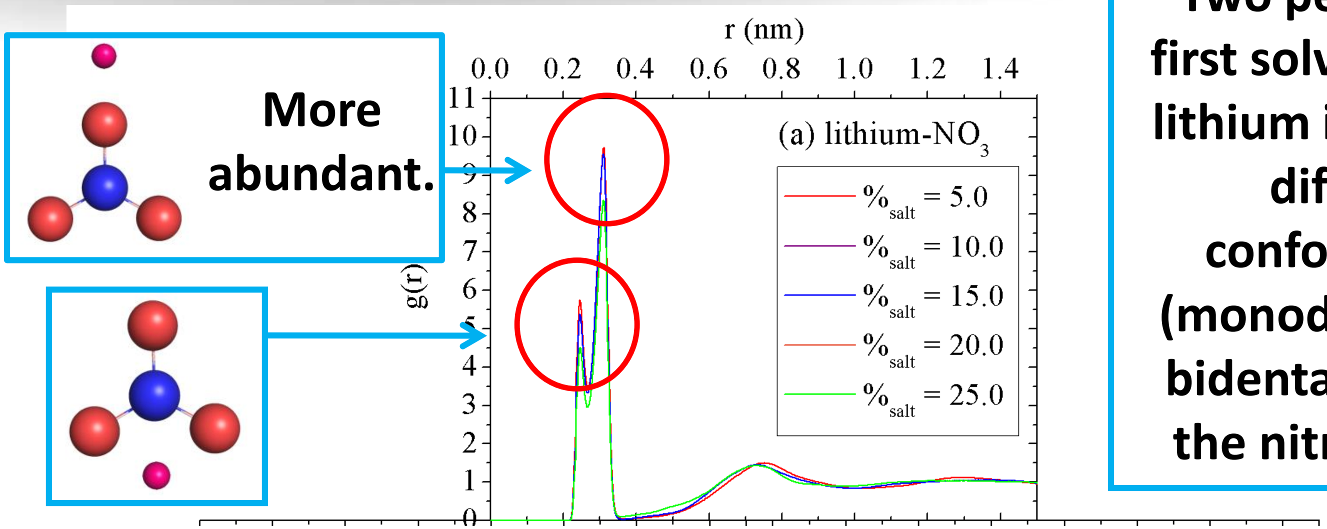

Two peaks in the first solvation shell: lithium ion has two different conformations (monodentate and bidentate) around the nitrate anion.

These distributions somehow reminds that of the calcite type structure characteristic of a crystal of lithium nitrate.

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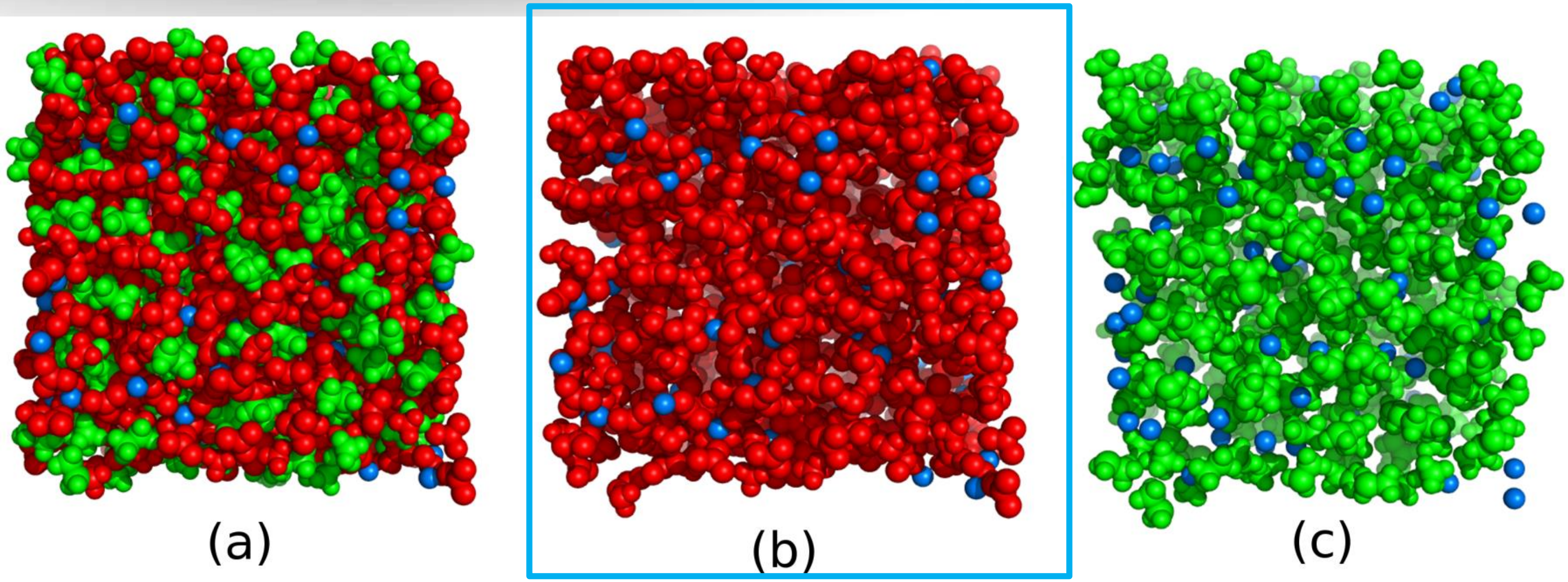
❖ Conclusion



whole system | **polar domains + lithium** | **apolar domains + lithium**

Salt cations are mainly located in the polar regions of the solution in a crystalline-like fashion

Great influence in the network of hydrogen bonds formed PILs.

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Thank for your attention

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