Recent Developments in the Thermodynamics of Ionic liquids

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Research Group AIM

Understanding & Fine Tuning
Thermophysical & Transport Properties

"Future & Today Challenge..."

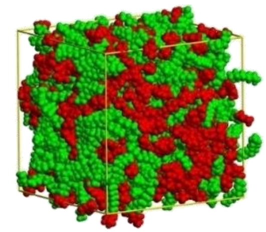
Alkyl Group Position (Isomerization)
Alkyl chain length
Group Substituion effects
Ils ..Mixtures

→

Materials
Soft/Regular Properties Change
Applications

Advantages:
- Predictable Thermal Stability
- Low Change in the Acidity/Basicity and Chemical Activity
- **Soft/ Regular** Properties Change

ThermPhys
Thermophysical Properties of Solids and Fluids Working Group



Thermodynamics of solid / liquid / gas

Enthalpies of formation (s/l)
(Combustion calorimetry)
(high precision solution-reaction calorimetry)

Entropies and Enthalpies of sub/vap (s/l)
(Knudsen effusion methods; static methods)
(Micro calorimetry)

p (*T*)

Solid → mesophases → Liquid → gas

Properties liquids/ solutions /solvation
(Density, viscosity, surface tension, speed of sound …etc)

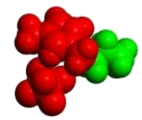
- **Heat capacities; enthalpies and entropies of fusion;**
- **Phase behavior; temperature of fusion**

(DSC, adiabatic calorimetry; drop calorimetry)

Gas phase ENERGETICS
(Quantum Chemical Calculations)

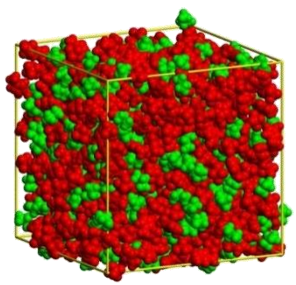
HOW Nanostructuration in ILs is reflected in their THERMODYNAMIC properties?

>Alkyl chain length

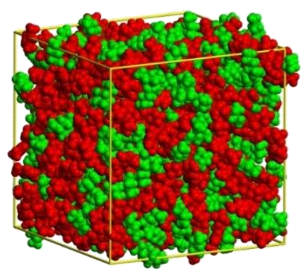


Red – Polar Network
Green – Non-polar domain

Segregation polar and **non-polar domains**



C_2mimPF_6



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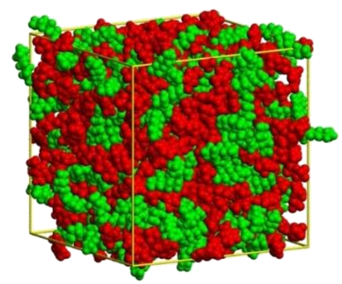
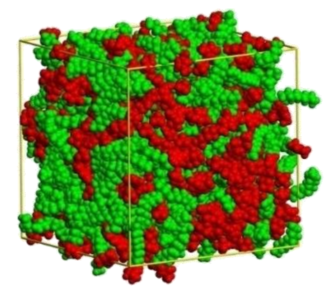


C_6mimPF_6



C_8mimPF_6

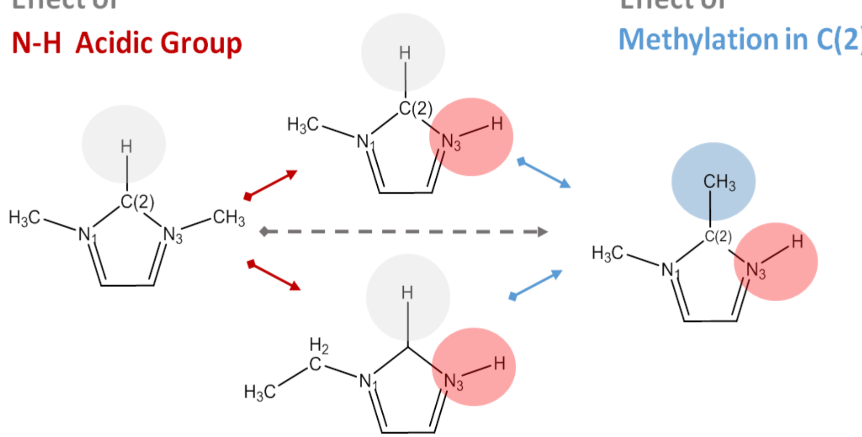
A.A.H. Pádua, J.N. Canongia Lopes, J. Phys. Chem. B 110 (2006) 3330.

HOW the isomerization in ILs is reflected in their THERMODYNAMIC properties?

PHYSICOCHEMICAL Properties

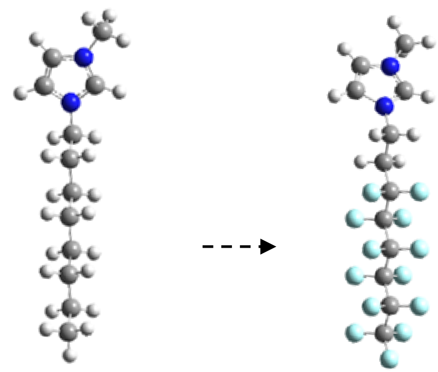
Effect of
N-H Acidic Group

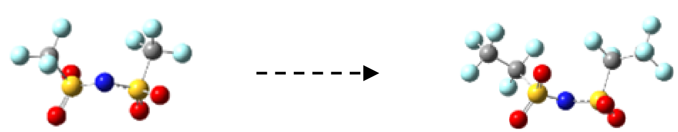
Effect of
Methylation in C(2)

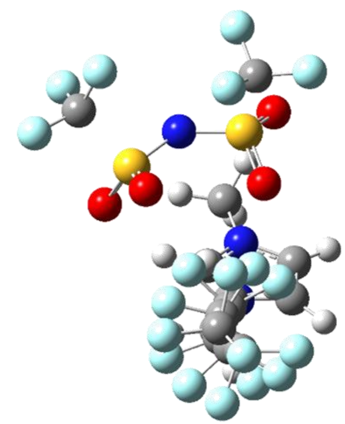


Density
Heat capacity
Refractive indices
Surface Tension
Viscosity
Thermal Behavior
Cohesive energy

HOW the Fluorination of ILs is reflected in their THERMODYNAMIC properties?



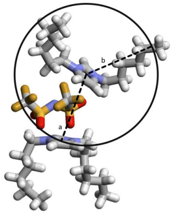


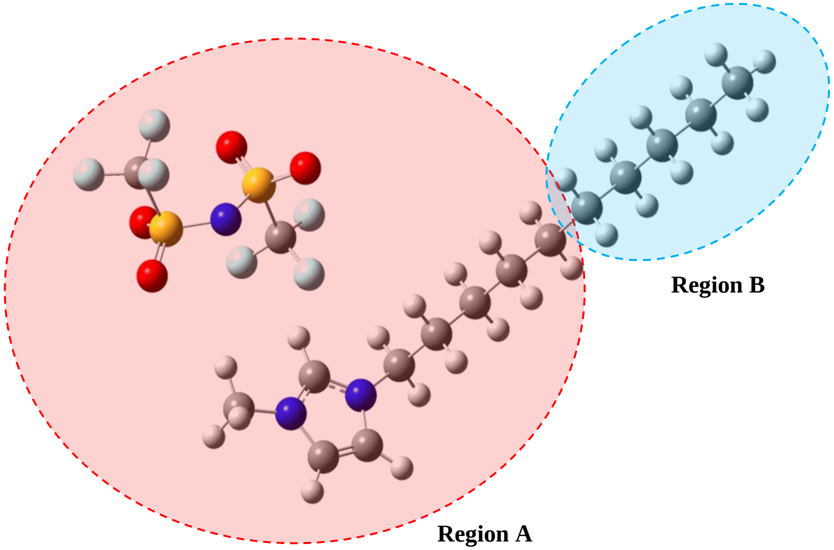


HOW the Nanostructuration in ILs is reflected in their
THERMODYNAMIC properties?
>Alkyl chain length

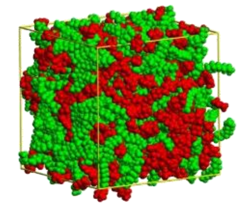
Region A
Electrostatics interaction

Region B
Low or Non-Electrostatics interaction

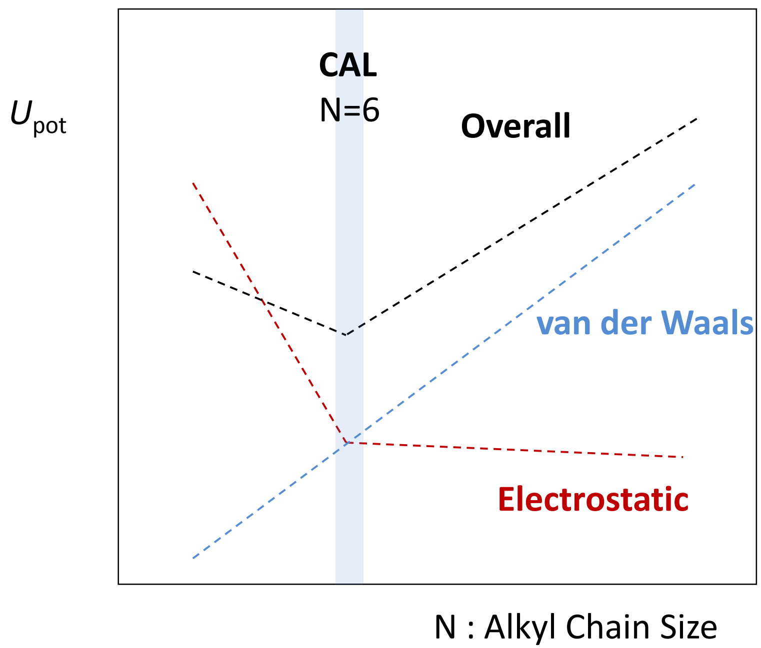


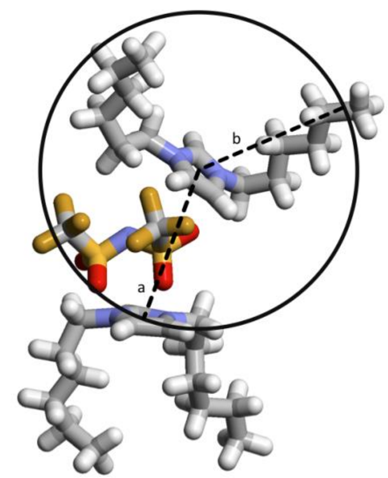


ThermPhys
Thermophysical Properties of Solids and Fluids
Working Group



TREND SHIFT ..... CAL ... Critical alkyl length



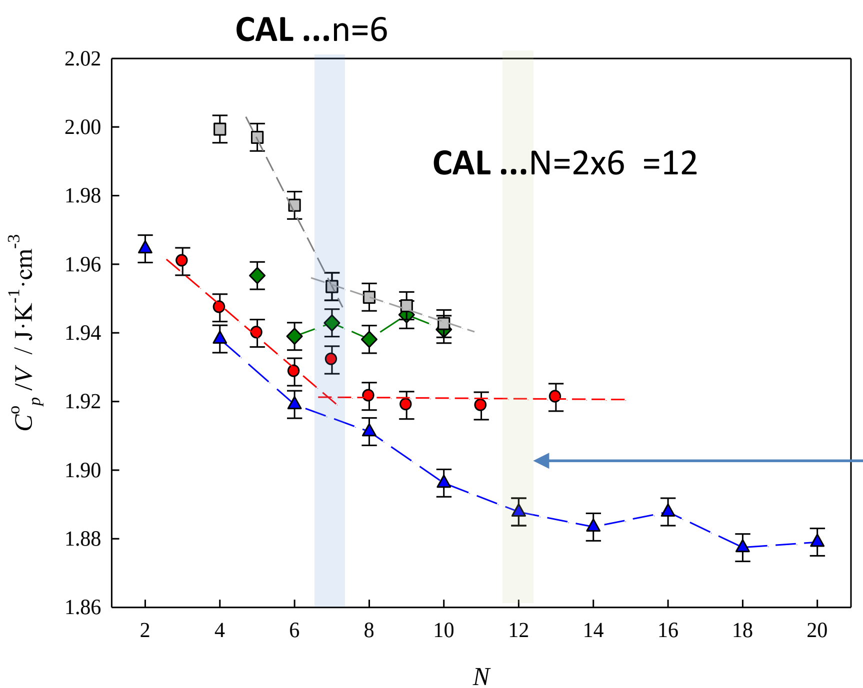


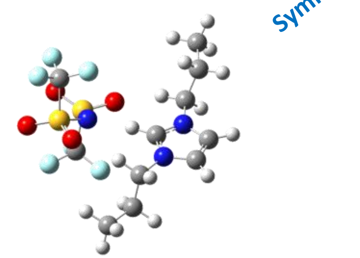
Journal of Physical Chemistry B **2014** *118,* 6885-6895
Phys. Chem. Chem. Phys., **2015**,17, 2560-2572

Heat Capacity ..Data

High-Precision **Heat Capacity** Drop Calorimeter

Heat Capacities of Ionic Liquids – $C_p\,/V$= f(N), T=298.15 K





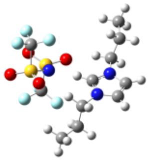
Alkyl Side Chain Length effect

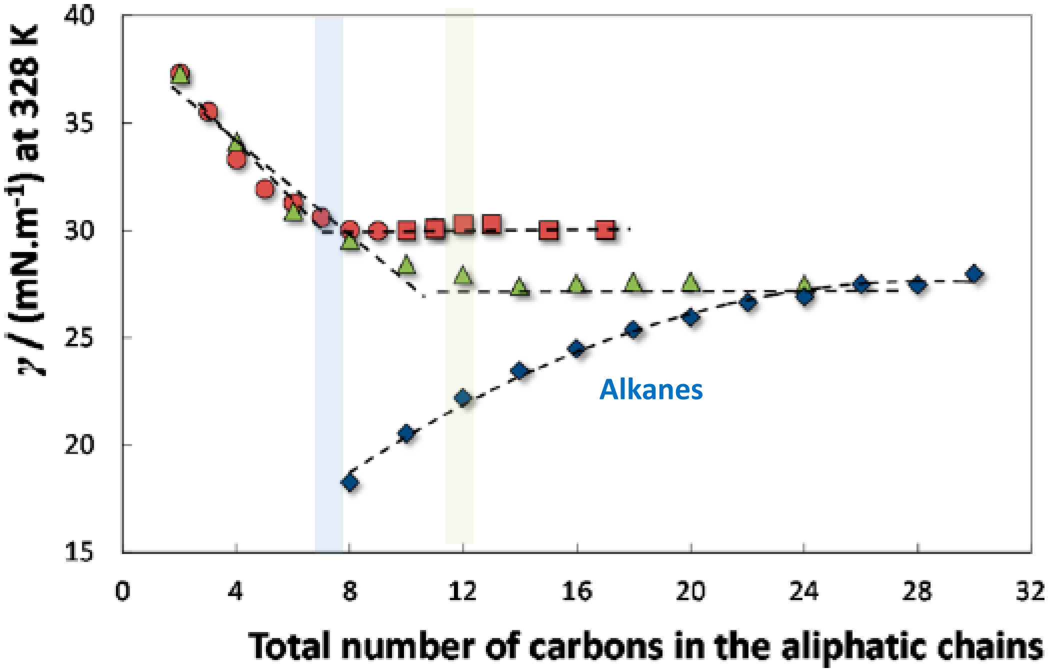
Rocha, Santos et al. J. Chem. Thermodyn 2012, 53, 140-143 (Paper III);
Rocha, Santos et al. J. Chem. Phys. 2013, 139, 104502 (Paper V);

Konicek, J.; Suurkuusk, J.; Wadsö, I. Chem. Scripta 1971, 1, 217-220; Suurkuusk, J.; Wadsö, I. J. Chem.Thermodynamics 1974, 6, 667-679
Santos et al. J. Chem. Thermodynamics 2011, 43, 1818-1823 (Paper I)

Surface tension ..Data

Surface tension = f(N(C))





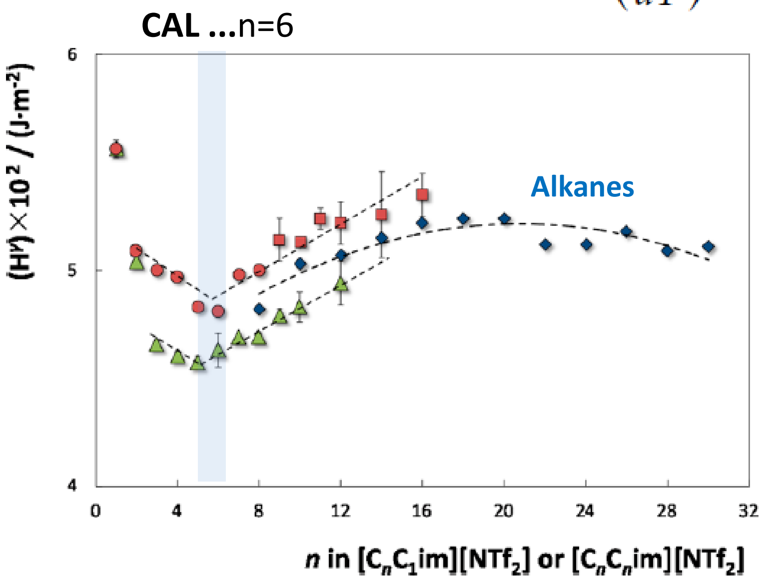
Langmuir 2014, 30, 6408−6418

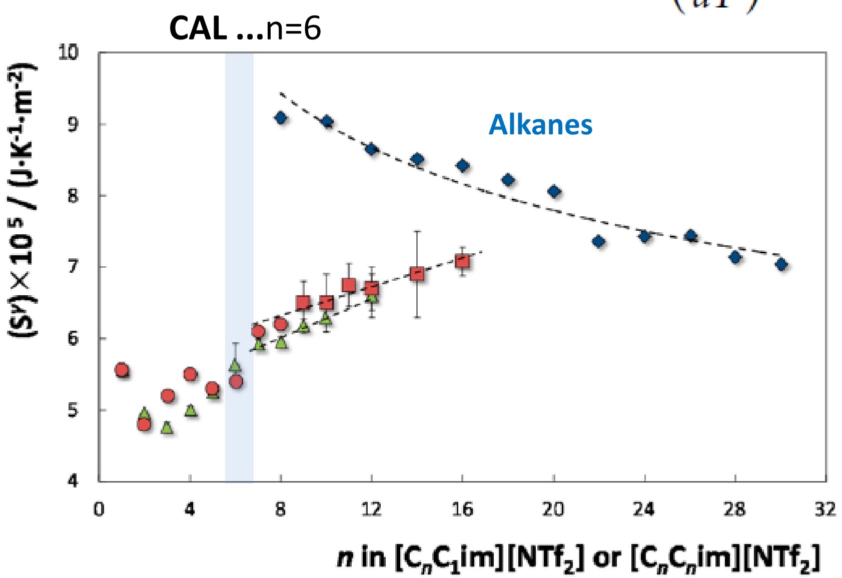
Surface tension ..Data

Surface tension = f(*N*(C))

$$H^{\gamma} = \gamma - T\left(\frac{d\gamma}{dT}\right)$$

$$S^{\gamma} = -\left(\frac{d\gamma}{dT}\right)$$

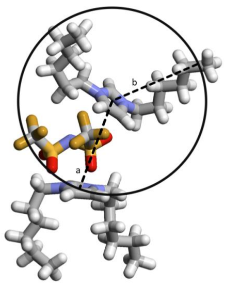




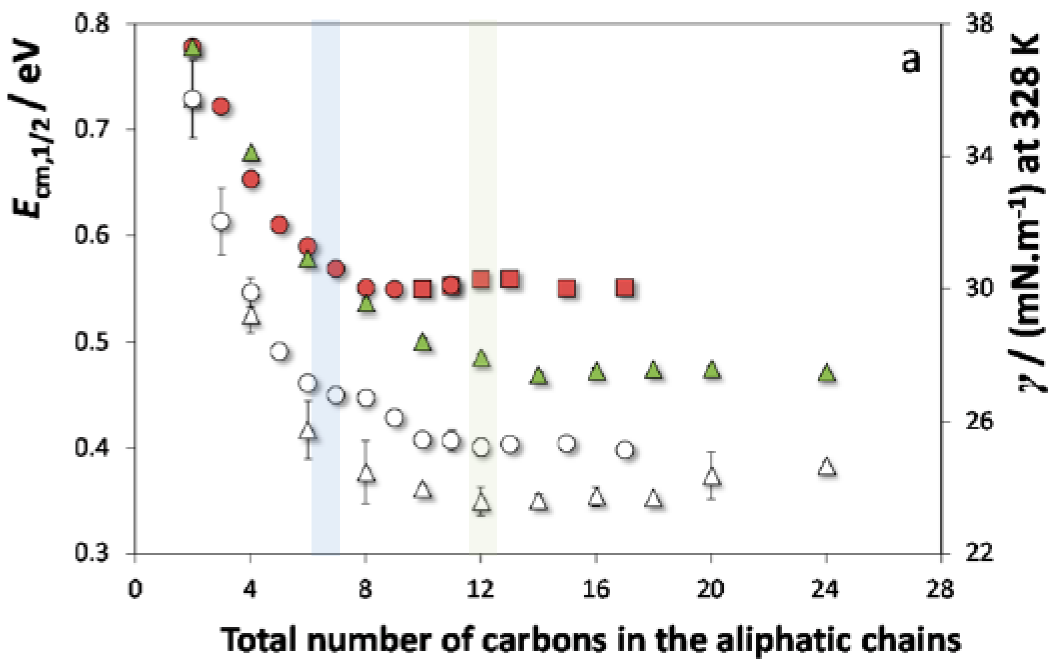
Langmuir 2014, 30, 6408−6418

(ESI-MS -MS) … Data

Electrospray ionization mass spectra (ESI-MS -MS)
Gas phase cation−anion relative interaction energy **= f(*N*(C))**



CAL …n=6



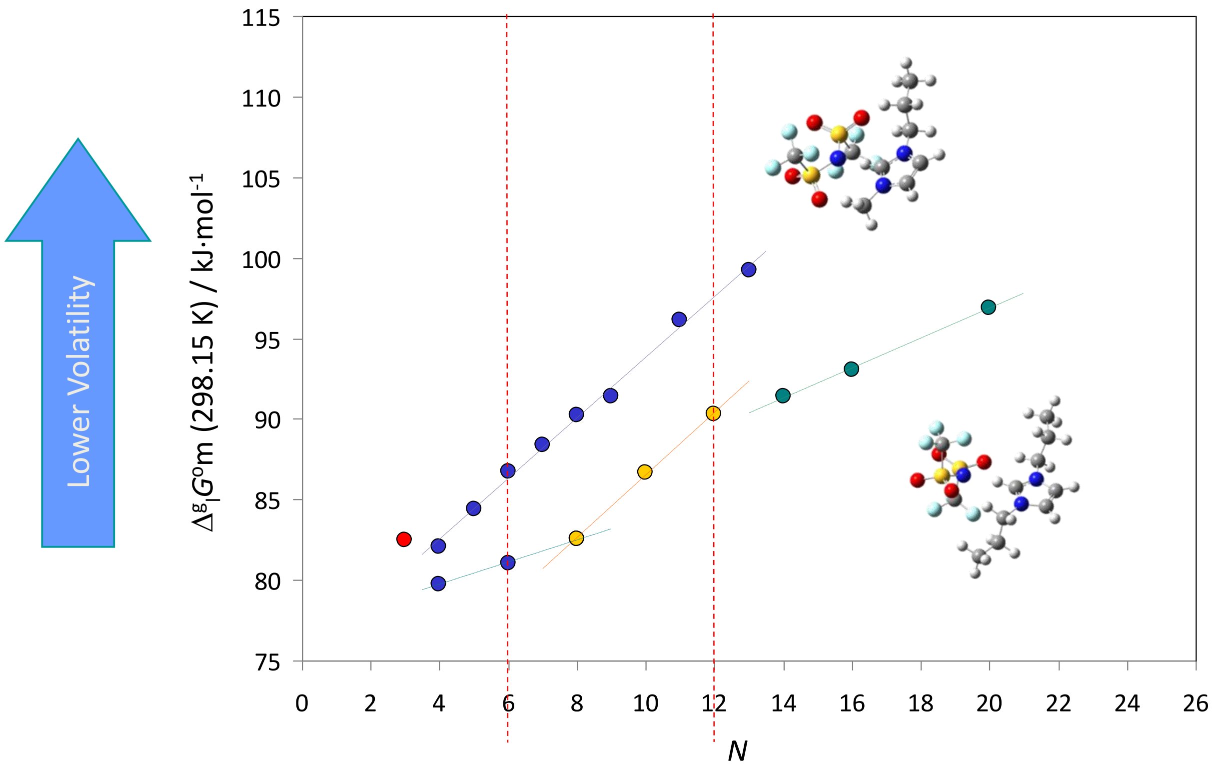
Langmuir 2014, 30, 6408−6418

ThermPhys
Thermophysical Properties of Solids and Fluids

Vapor pressure… Data

Volatility …$\Delta^{g}_{l}\, G^{o}_{m}$ (298.15 K) = f(N(C))

$[C_{N/2}C_{N/2}im][NTf_2]$ vs $[C_{N-1}C_1im][NTf_2]$



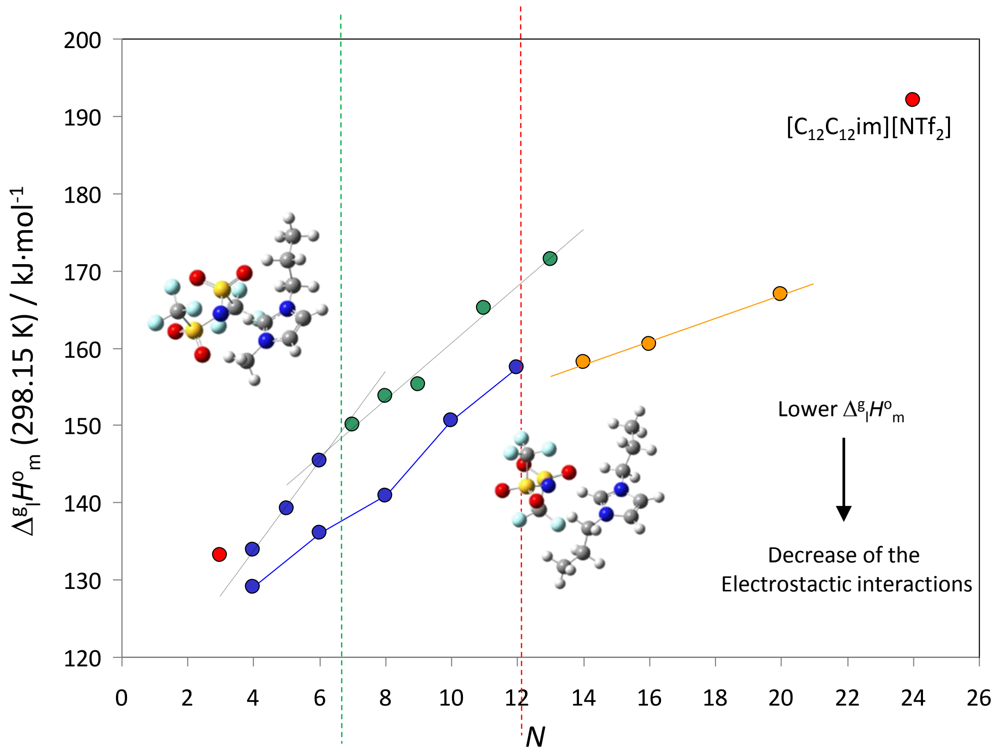
M. A. A. Rocha et al. / *J. Phys. Chem. B*, **2011**, *115* (37), pp 10919–10926

M. A. A. Rocha et al. / *J. Phys. Chem. B*, **2012,** *116* (35), pp 10922–10927

Vapor pressu… Data

Enthalpies of Vaporization …$\Delta^g_l H^o_m$ (298.15 K) = f(N(C))

$[C_{N/2}C_{N/2}im][NTf_2]$ vs $[C_{N-1}C_1im][NTf_2]$



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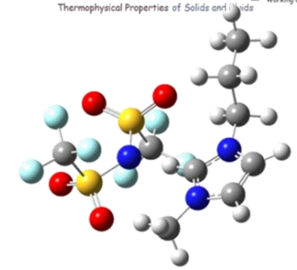
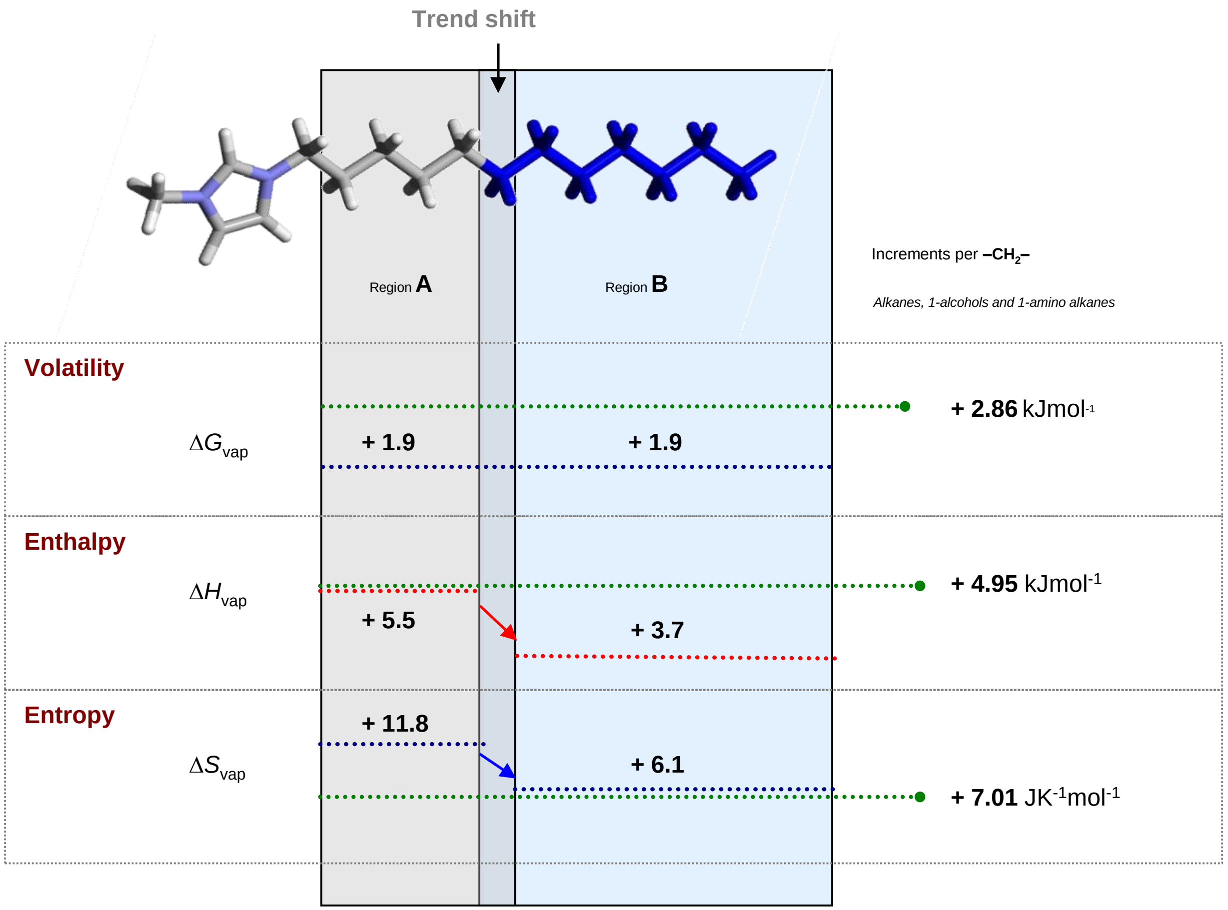
ThermPhys
Thermophysical Properties of Solids and Liquids



Vapor pressure… Data

Volatility Study of [C_nC1im][NTf_2] (n = 2 – 12)…



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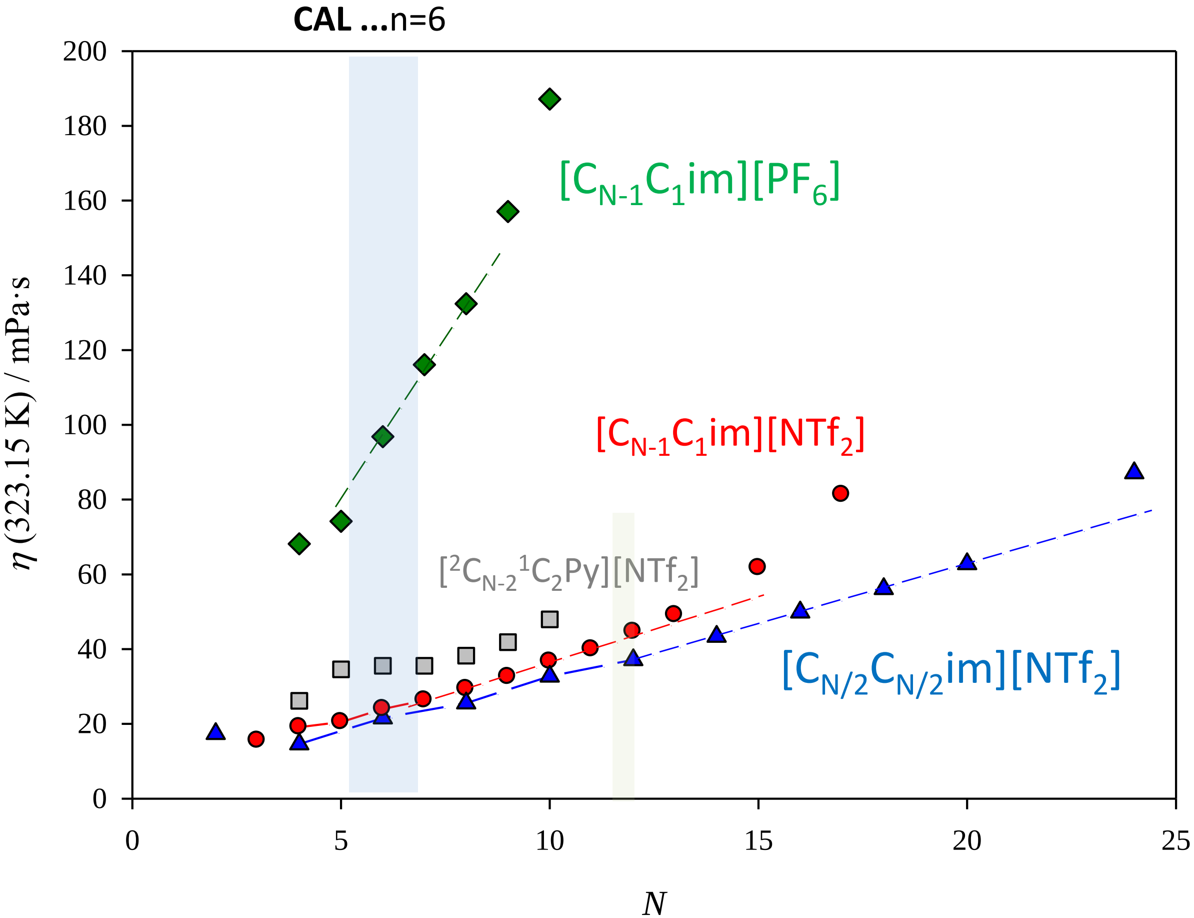
M. A. A. Rocha et al. / *J. Phys. Chem. B*, **2012,** *116* (35), pp 10922–10927

Viscosity Data

ThermPhys

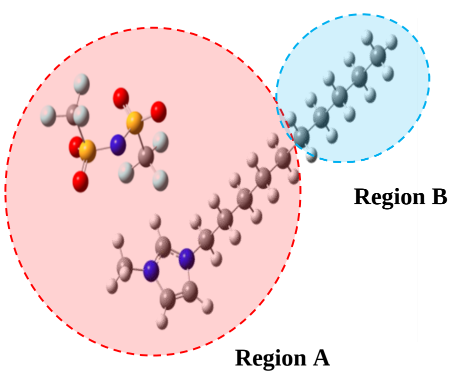
Viscosities of Ionic Liquids – η = f(N), T=323.15 K



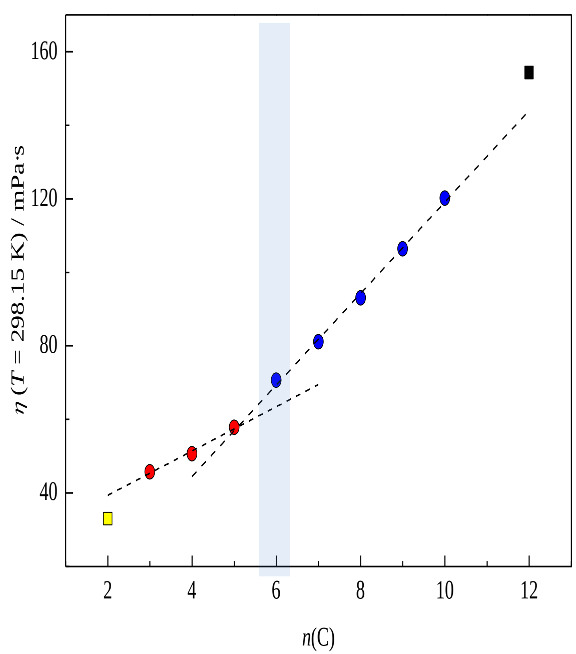
ThermPhys

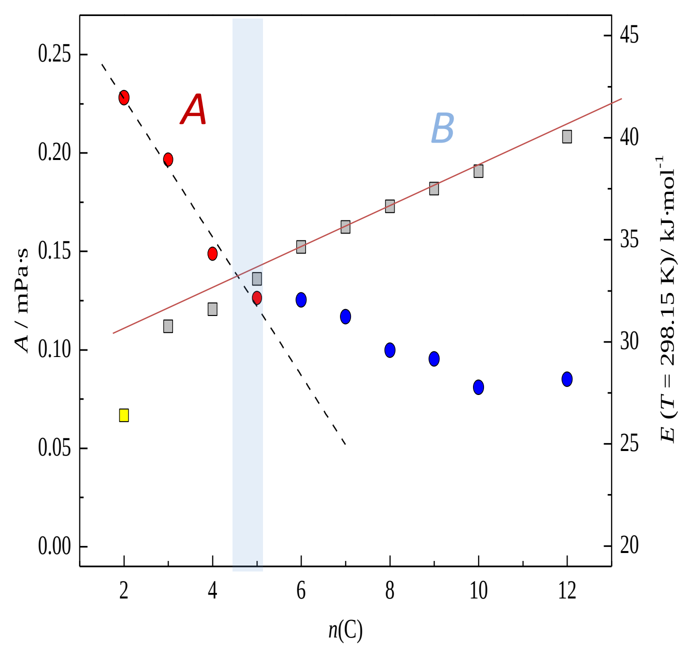
Viscosity Data

Vogel-Tammann-Fulcher Equation (VTF)… $\eta = A \cdot \exp[B/(T-C)]$



η





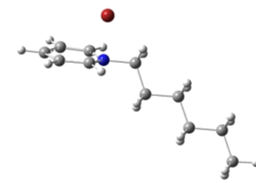
Journal of Physical Chemistry B (2013) 117, 10889-10897

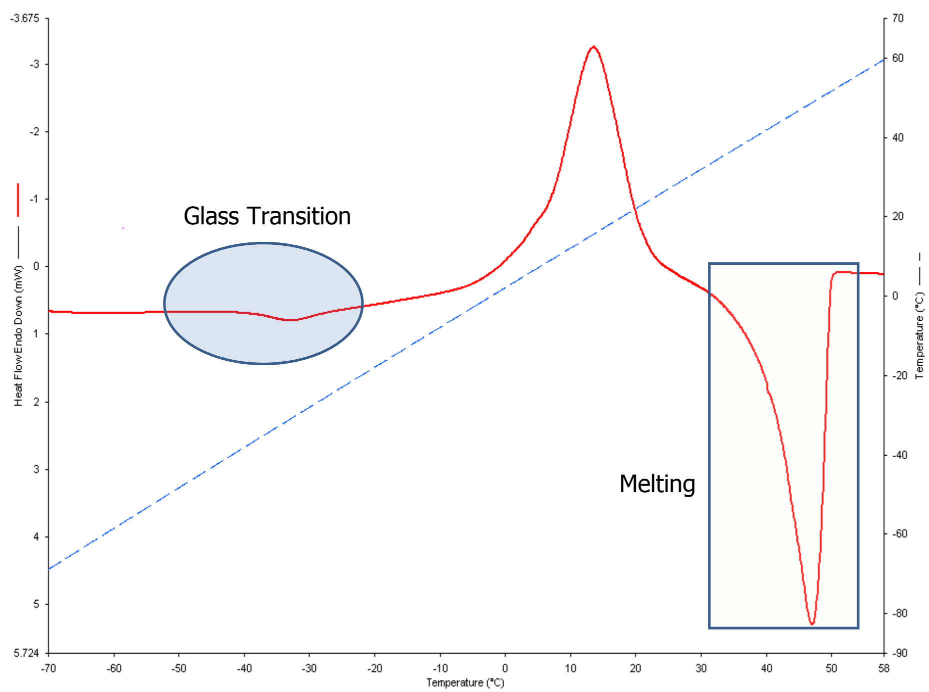
Thermal Behavior

Differential Scanning Calorimetry

Thermal & Phase Behavior $[C_6Py]^+Br^-$ Quenching at -100ºC; heating at 5 K·min^{-1}

Cool Crystallization, **Beta @ 5ºC·min-1**





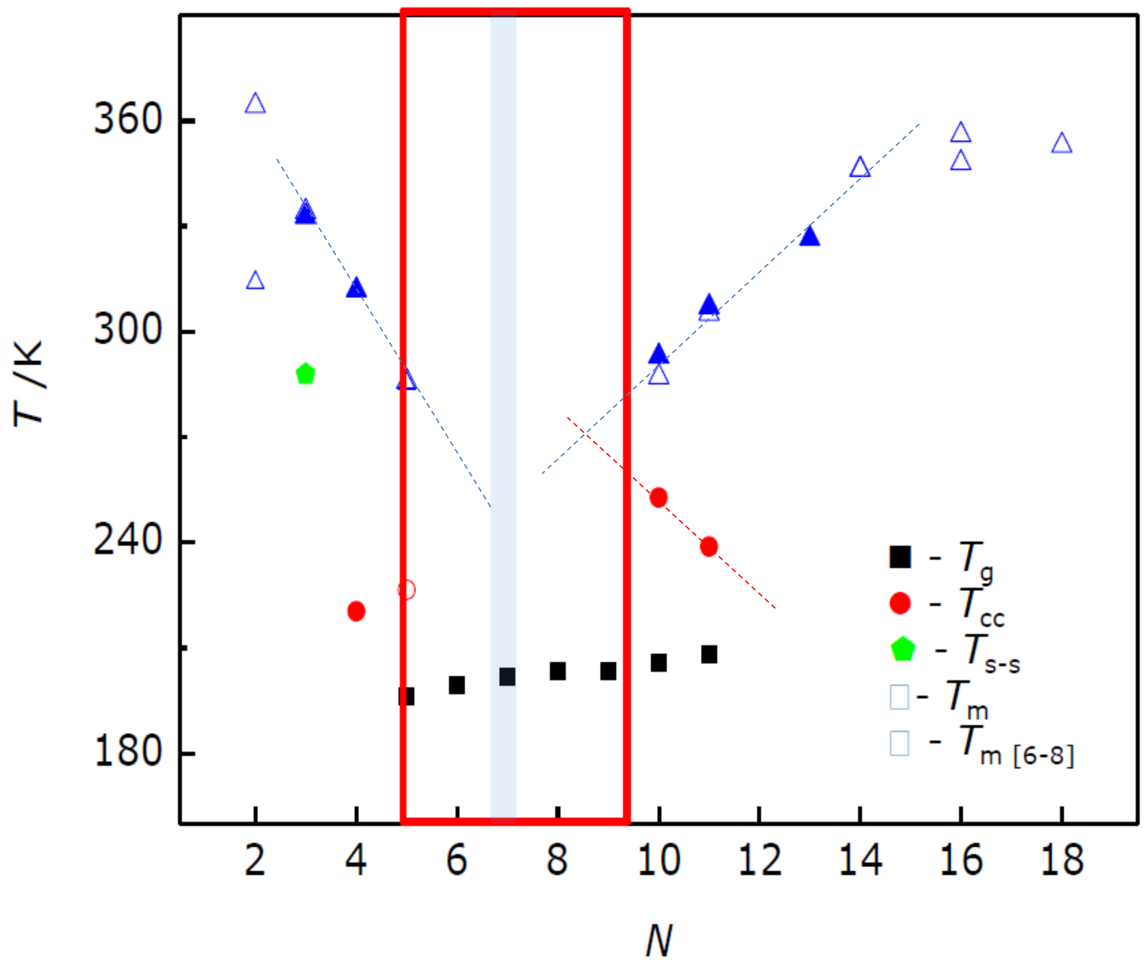
Thermal Behavior

ThermPhys
Thermophysical Properties of Solids and Fluids Working Group

Differential Scanning Calorimetry

CAL …n=6

Thermal & Phase Behavior ….
$C_nC_1$im [PF6]



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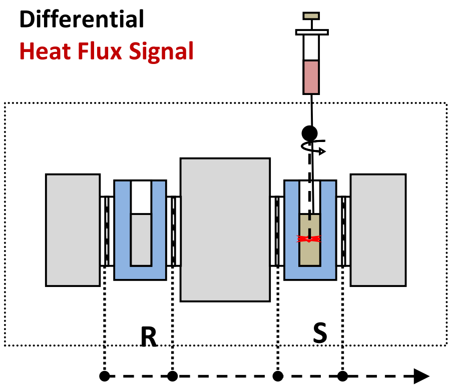
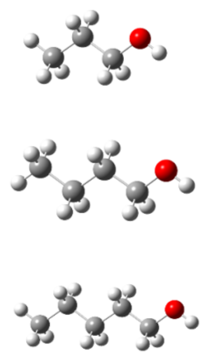
What solvation says about the Nanostructuration in ILs?

Isothermal Titration Calorimetry , ITC

Solvation of alcohols in Ionic Liquids

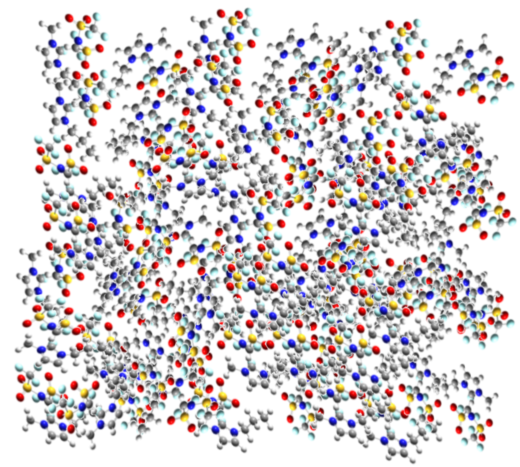


Alcohols



Solvation

Ionic Liquids

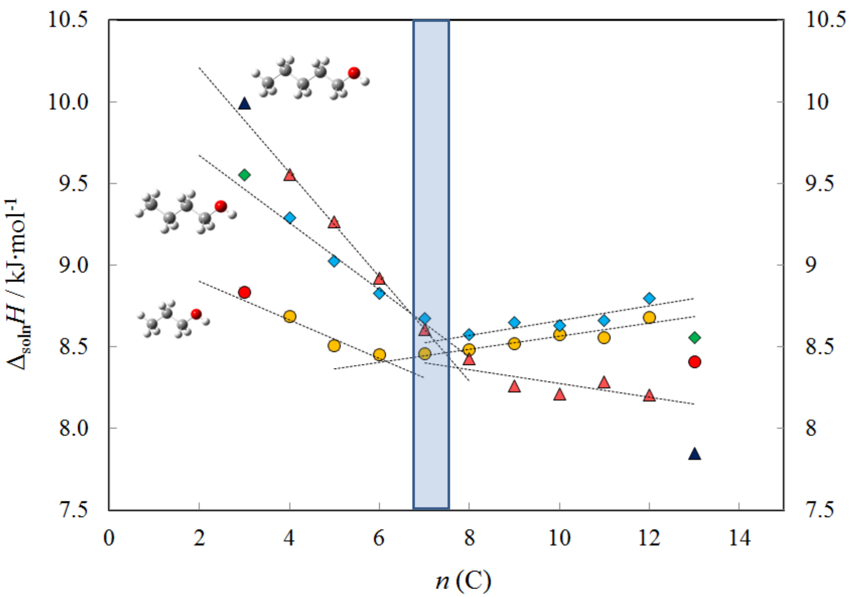


MOLECULAR PROBES

What solvation says about the Nanostructuration in ILs?

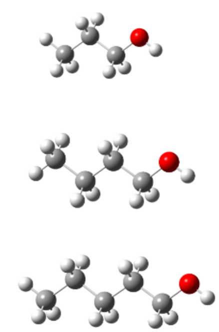
Solvation of **alcohols in Ionic Liquids** (ITC)

Trend Shift .. $C_6C_1imNTf_2$

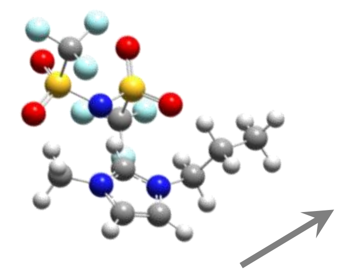


Alcohols

MOLECULAR PROBES



$[C_{N-1}C_1im][NTf_2]$

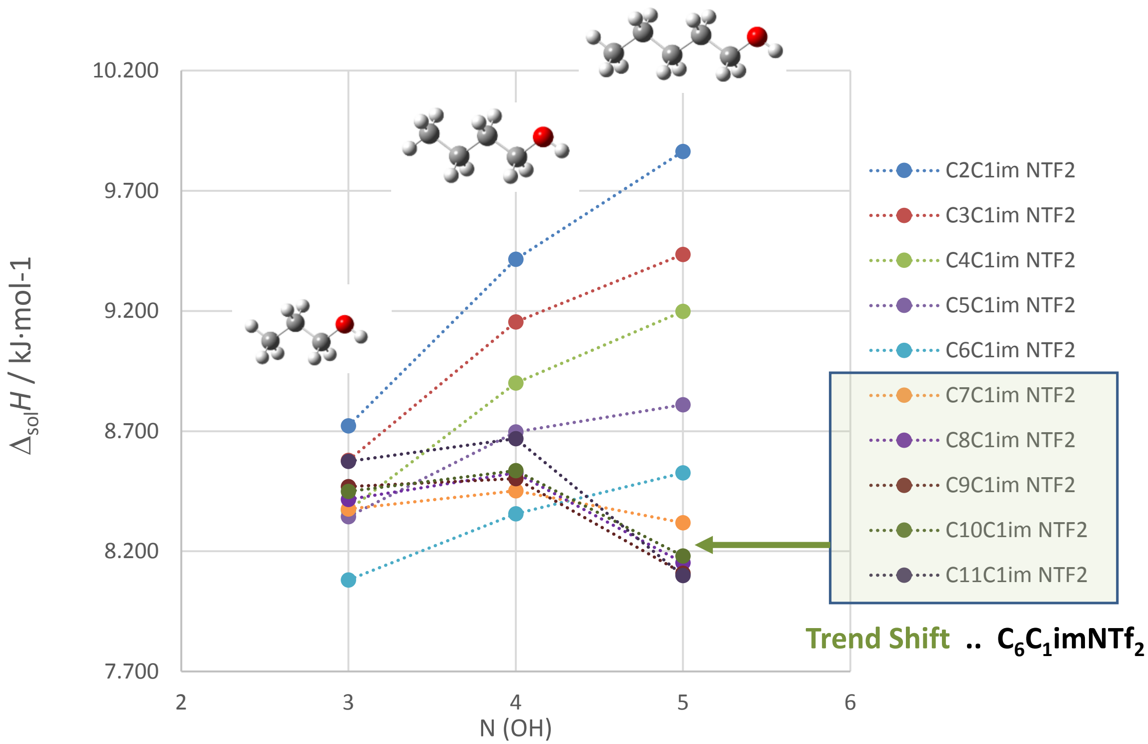


Alkyl side chain length (N = 3 – 13)

ThermPhys
Thermophysical Properties of Solids and Fluids Working Group

What solvation says about the Nanostructuration in ILs?

Solvation of **alcohols in Ionic Liquids** (ITC)

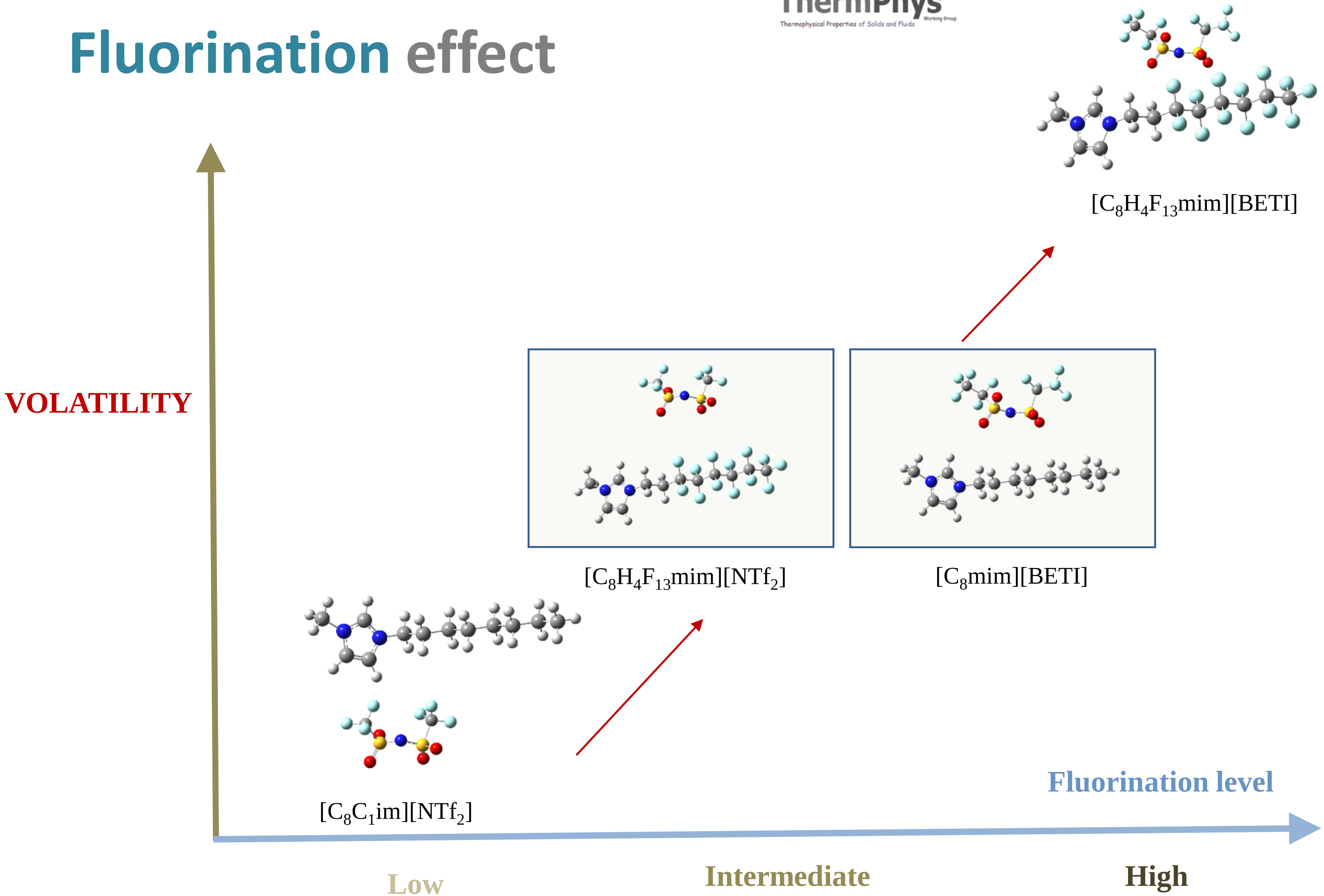


Alcohols

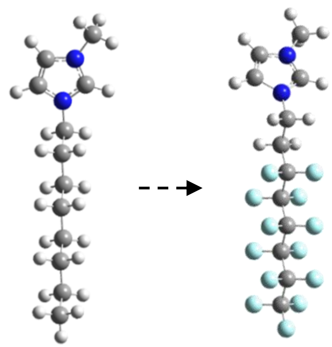
MOLECULAR PROBES

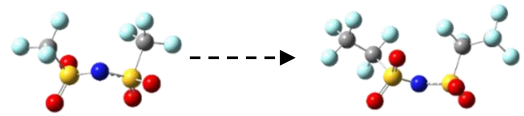
Trend Shift .. $C_6C_1imNTf_{2<}$

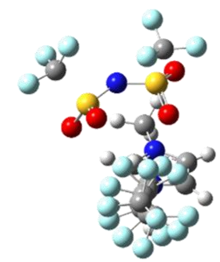
Fluorination effect



Fluorination effect







e.g. volatility

Enthalpic
(contribution)

Enthalpy INCREASE
(> less volatile)

Entropic
(contribution)

Entropy INCREASE
(> more volatile)

Entropically DRIVEN
(more volatile)

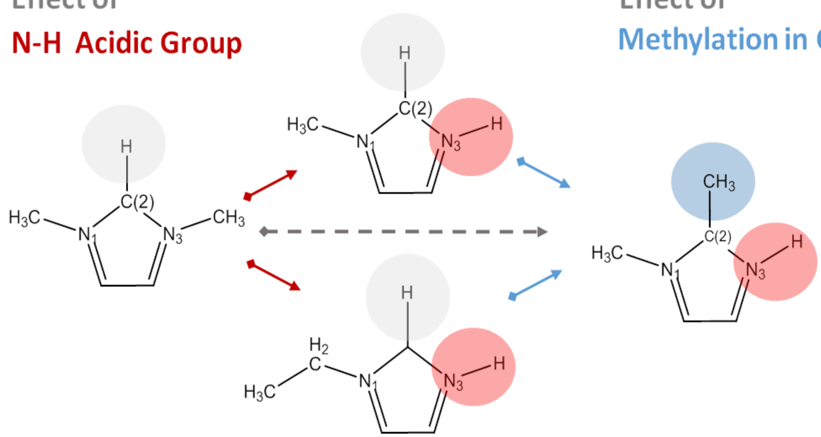
Volatility
overall

HOW the isomerization in ILs is reflected in their THERMODYNAMIC properties?

PHYSICOCHEMICAL Properties

Effect of
N-H Acidic Group

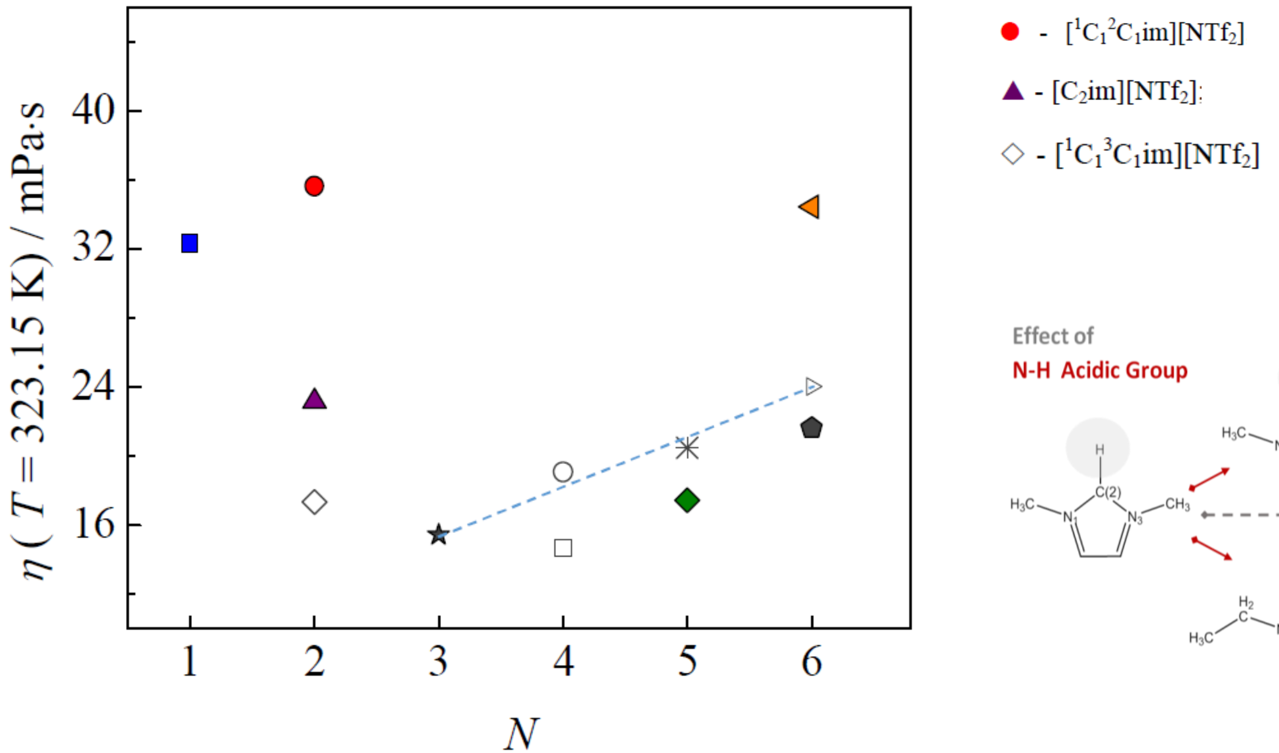
Effect of
Methylation in C(2)

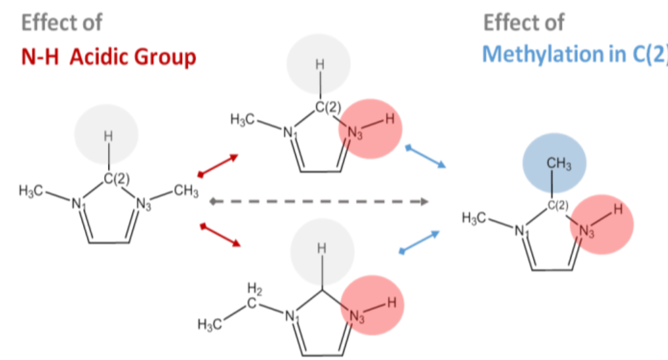


- Density
- Heat capacity
- Refractive indices
- Surface Tension
- Viscosity
- Thermal Behavior
- Cohesive energy

HOW the isomerization in ILs is reflected in their THERMODYNAMIC properties?

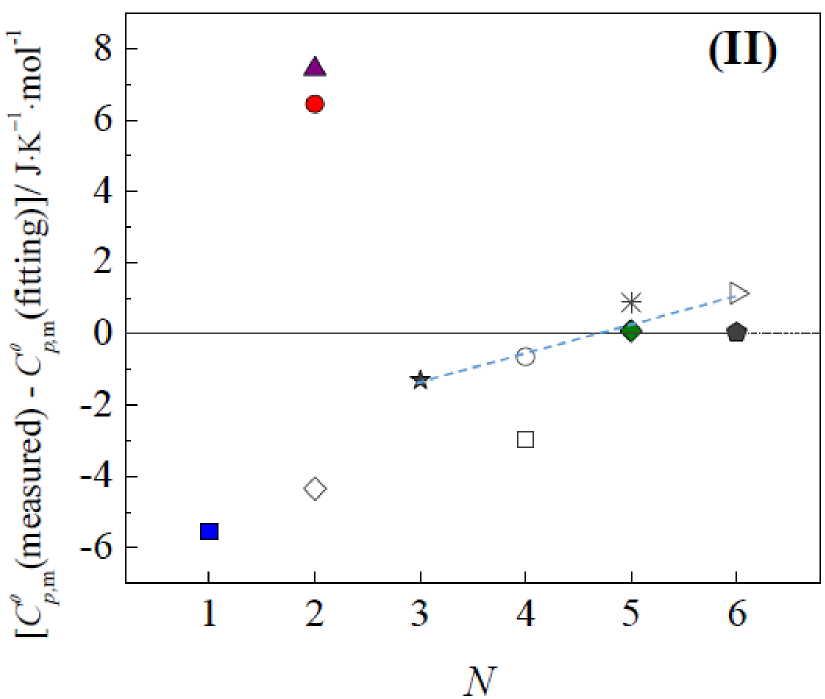
Viscosity





HOW the isomerization in ILs is reflected in their THERMODYNAMIC properties?

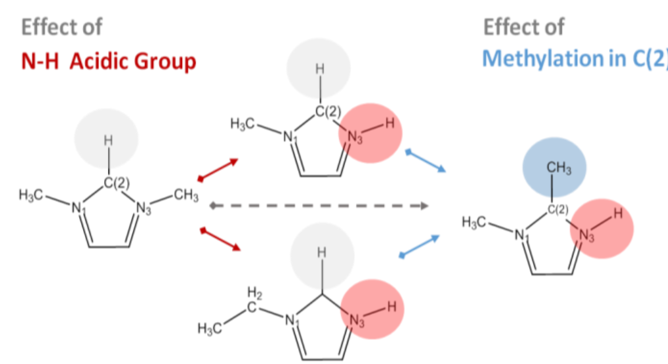
Heat Capacity



● - $[^1C_1{}^2C_1im][NTf_2]$

▲ - $[C_2im][NTf_2]$;

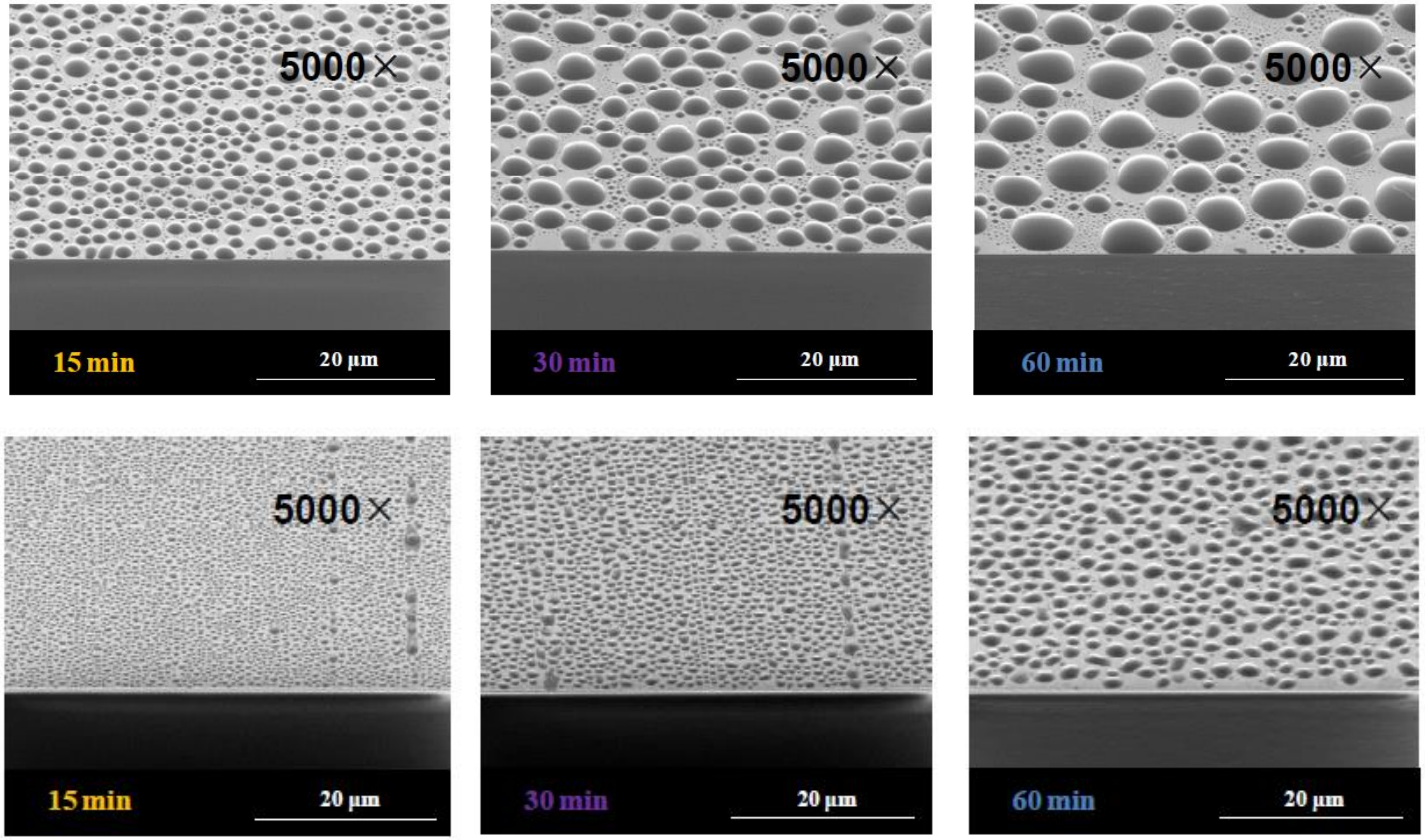
◇ - $[^1C_1{}^3C_1im][NTf_2]$



HOW the THERMODYNAMIC properties of ILs
are reflected in their application and functionality?

Thin Film ...Vacuum deposition in a ITO surface
Size increase and coalescence Nano size drops ... Why & How?

SEM



$C_2mimNtf_2$

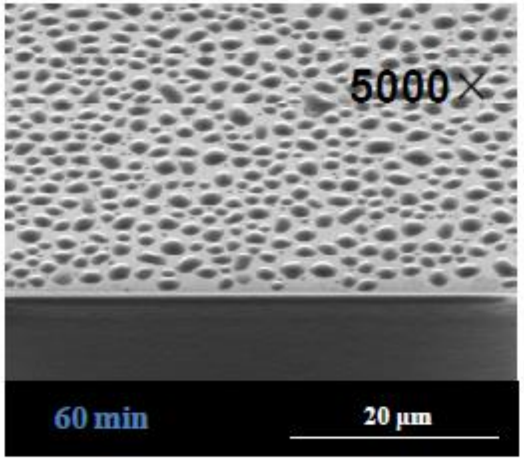
$C_6mimNtf_2$

PHYSICAL CHEMISTRY CHEMICAL PHYSICS (2014) 16, 19952-19963

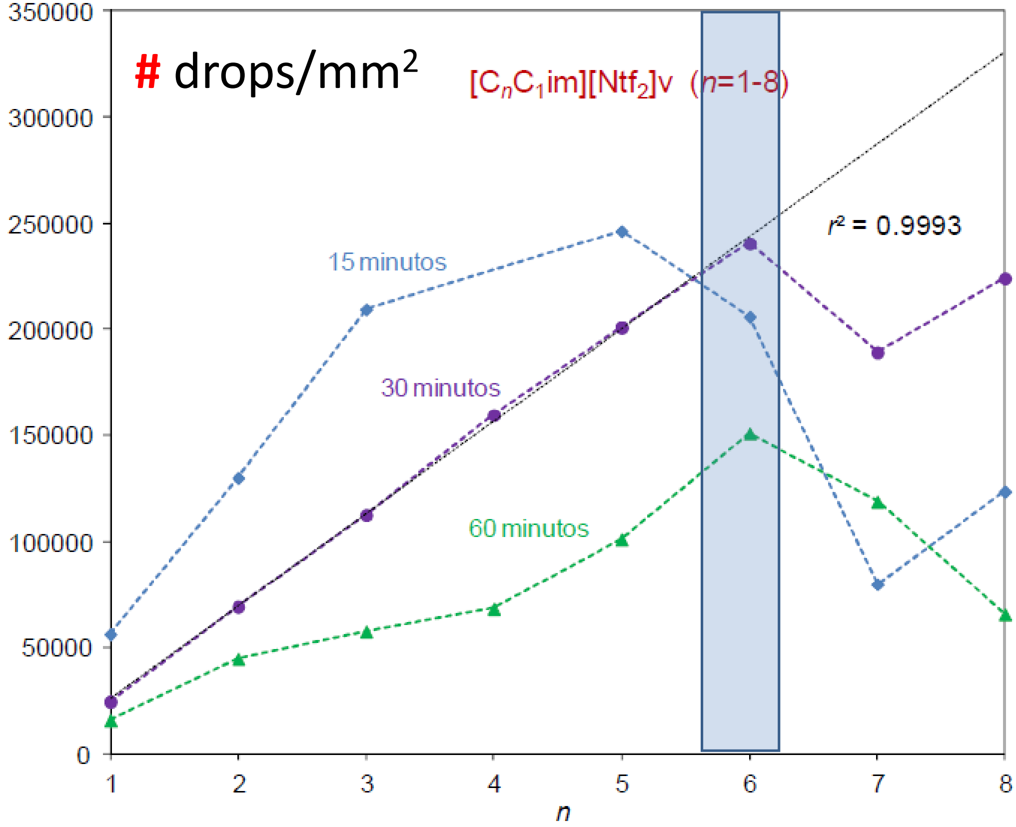
HOW the THERMODYNAMIC properties of ILs are reflected in their application and functionality?

Thin Film ...Vacuum deposition in a ITO surface

Size increase and coalescence Nano size drops ... Why & How?



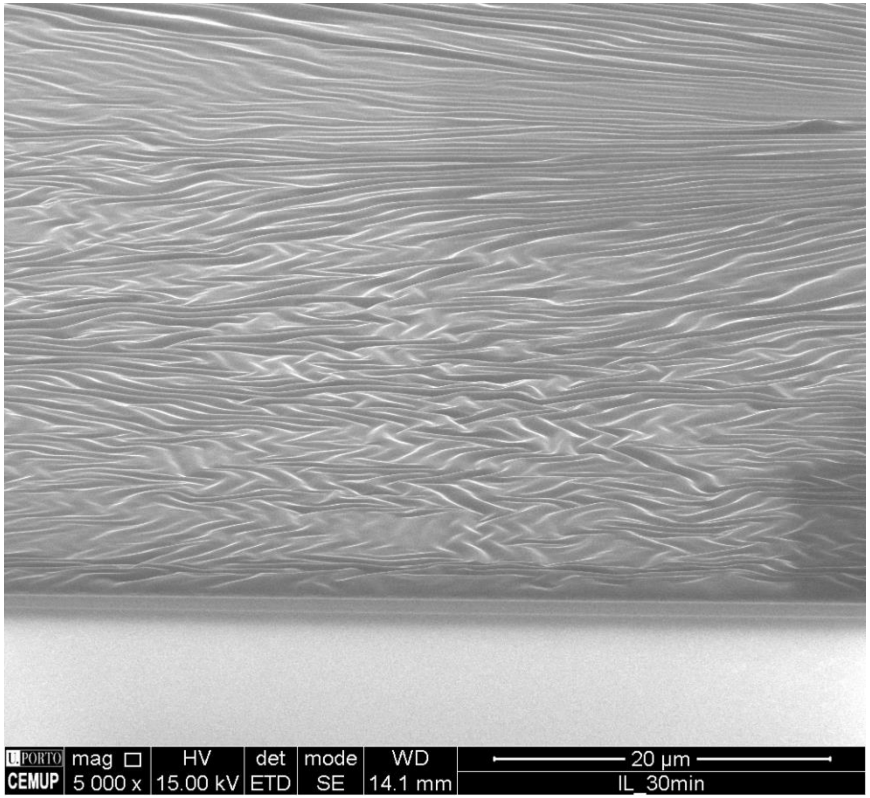
Trend Shift .. $C_6C_1imNTf_2$



HOW the THERMODYNAMIC properties can
help the liquid textures (WAVE parterns) ...of IL thin films

ILs on thin film on a ITO surface !!!!!

Thickness/ viscosity / surface tension >…… (T, P)



THANK YOU

http://ptsensethermphys.wix.com/thermphysgroup

Some extra/support slides …..

"Recent developments in the thermodynamics of ILs"

Luís M. N. B. F. Santos

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Ionic Liquids have gained increasing attention due to their potential as alternative solvents, new materials processing, developing of new functionality materials, as catalysts, among others. The increasing interest in Ionic liquids (ILs) are due as well, to their unique features resulting from the type of cohesive interaction, charge distribution, structuration, polar network and apolar domains, which lead to many interesting and unusual physical and transport properties. The molecular structure and supramolecular organization of an ionic liquid is complex, comprising polar and non-polar domains that is reflected in the complexity of the thermodynamic properties of ILs and ILs mixtures. The trend shift along the alkyl series, founded in the thermodynamic properties of several ILs series was related to the structural segregation in the liquid after a critical alkyl length (CAL) is attained. This presentation will be focused in analysis and short review of the state of art concerning the experimental thermodynamics studies of ILs, including their temperature dependence: thermal behavior (glass transition, crystallization temperatures/profile, melting temperature, enthalpies and entropies of fusion); heat capacities; cohesive energies; surface tension; densities; viscosities; solvation etc. The analysis of the thermodynamics data based in the effect of the cation and anions morphologies as well as, along the alkyl chain size have been used to give support/explore the nanostructuration interpretation and effect on the ionic liquid properties and unique features as a solvent and material.

Lecture ..Plan /Ideias/fundamentals

Density
(trends; information concerning the organization at the surface; thin film stability & morphology);
Heat capacities
(trends; group method contribution; solid & liquid differentiatin);
Thermal behavior
(glass transition, crystallization temperatures/profile, melting temperature, enthalpies and entropies of fusion);
Cohesive energies/energetics
(phase stability; trends; volatility; base to the simulation & modelation)
Interface/Surface tension
(enthalpy and surface formation trends; information concerning the organization at the surface; thin film stability & morphology);
Viscosities
(trends; energy barriers; cohesive energy; anion / cation / substituent effect; hydrogen bond; symmetry);
Solution & Solvation
(molecular probes; interaction enthalpies; cavitation; Nano structuration; hydrogen bond; symmetry);
ILs mixtures
(phase diagrams; excess properties; interface properties; structuration);
Fluorination effect
(additional new phase & nano structuration; cohesive energy; interface properties & structuration);
Protic … to Aprotic landscape! Ionic liquids
(speciation problem; acid-base equilibria; composition !; cohesive energy & volatility meaning).

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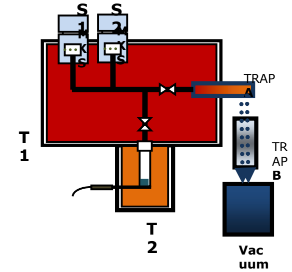

Static Apparatus

M. J. S. Monte, L. M. N. B. F. Santos, M. Fulem, J. M. S. Fonseca, C. A. D. Sousa, *J. Chem. Eng. Data,* 51 (**2006**) 757-766.

Two **MKS** Baratron Capacitance Manometers 631A (Calibrated NIST)

[0.4 - 133 Pa (423 K) ; 4 - 1333Pa (473 K)]

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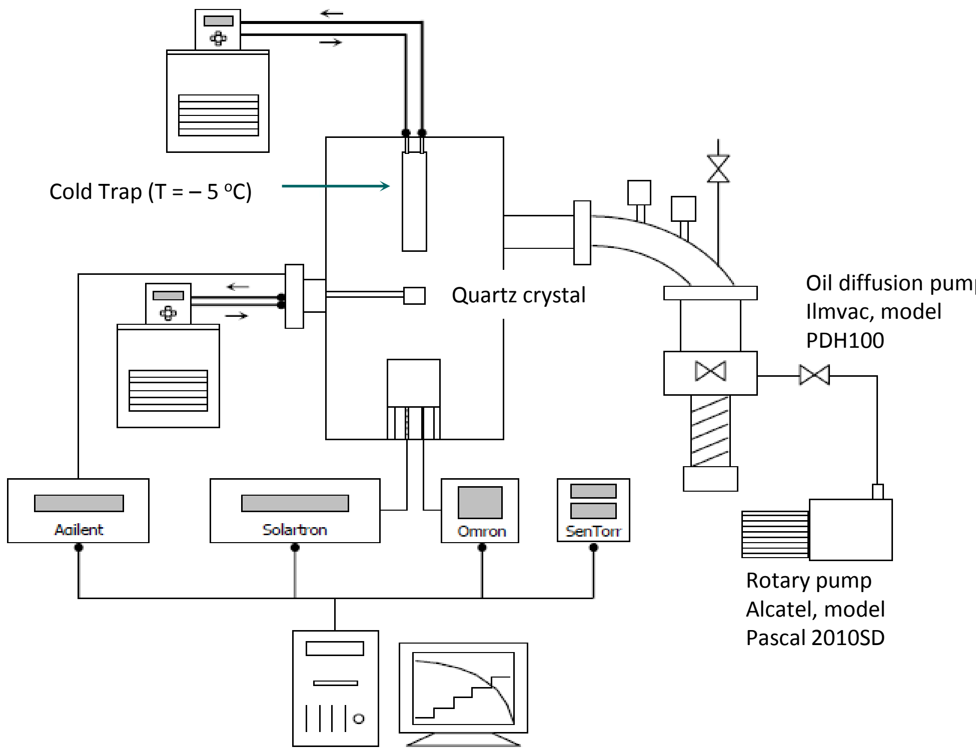
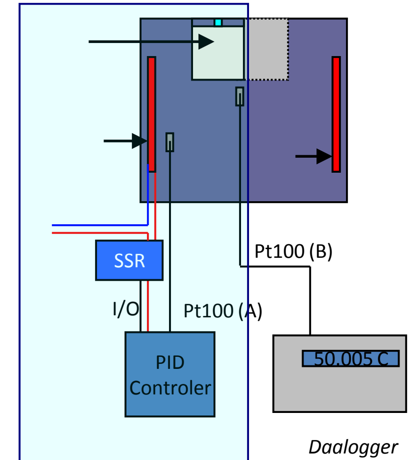
Knudsen Effusion Methods

Knudsen effusion apparatus combined with a quartz crystal microbalance - Schematic view





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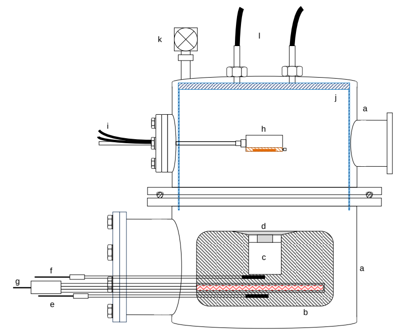
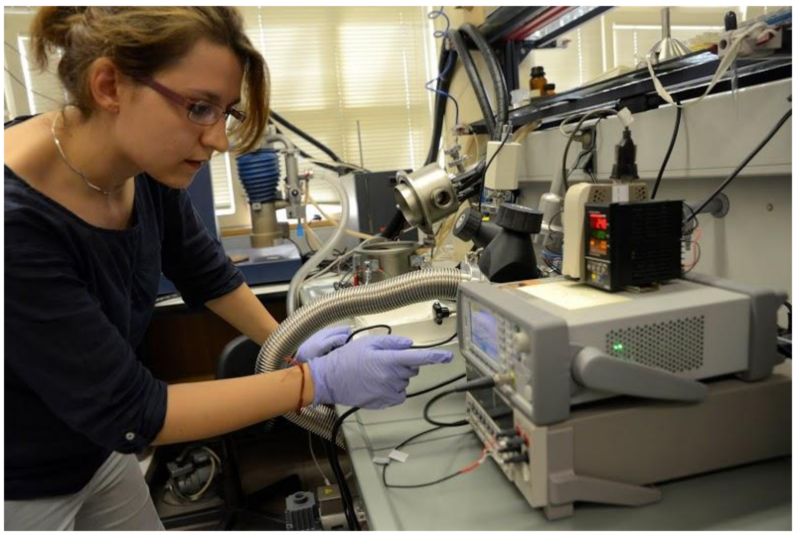
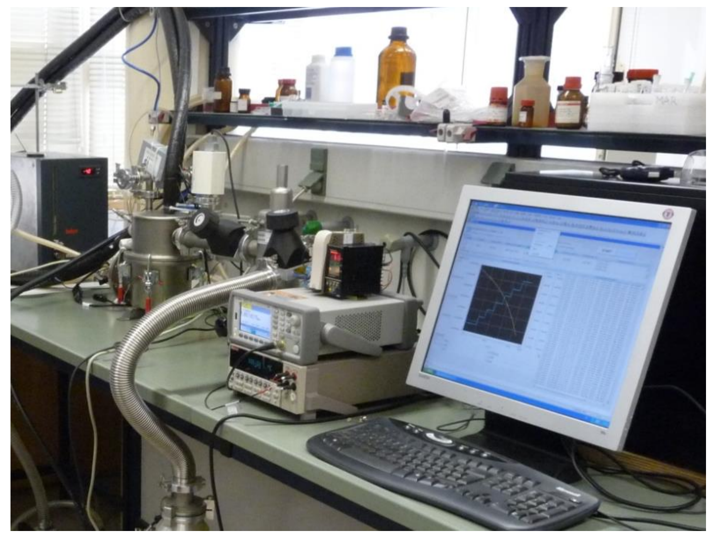


Knudsen Effusion Methods

Knudsen effusion apparatus combined with a quartz crystal microbalance





high vacuum <10^{-6} mbar.

Internal cold trap (**<** background sign, **>** the repeatability).

QCM positioned above the effusion cell.

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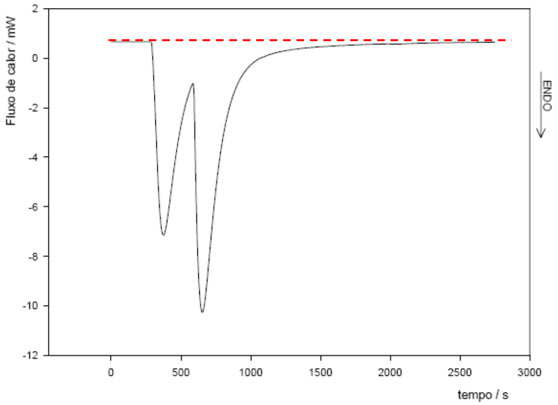
Calvet Microcalorimetry drop method

Direct determination of $\Delta^{g}_{cr/l}H^{o}_{m}$

L. M. N. B. F. Santos, B. Schröder, O. O. P. Fernandes, M. A. V. Ribeiro da Silva, *Thermochim. Acta,* 415 (**2004**) 15-20.



Capilary tubes: 20 – 30 mg
Sample: 3 – 5 mg

$$\Delta^{g}_{cr/l}H^{o}_{m}\ (T=298.15\ \mathrm{K}) = \Delta^{g,\,T}_{cr/l,\,298.15\ \mathrm{K}}H^{o}_{m} - \Delta^{T}_{298.15\ \mathrm{K}}H^{o}_{m}(g)$$

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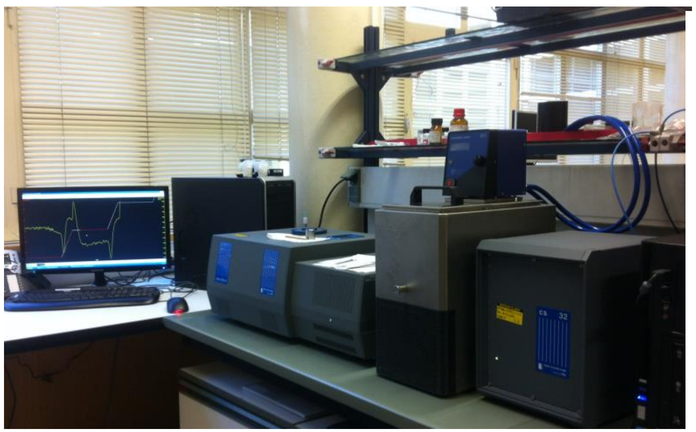
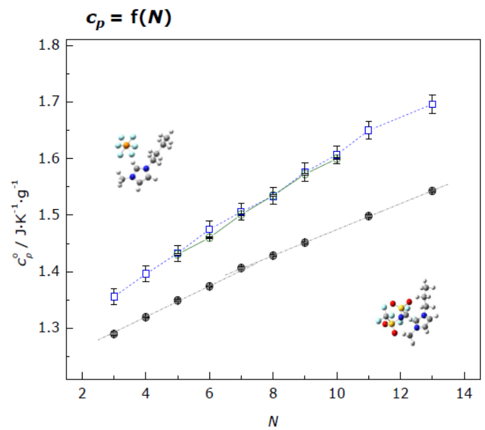
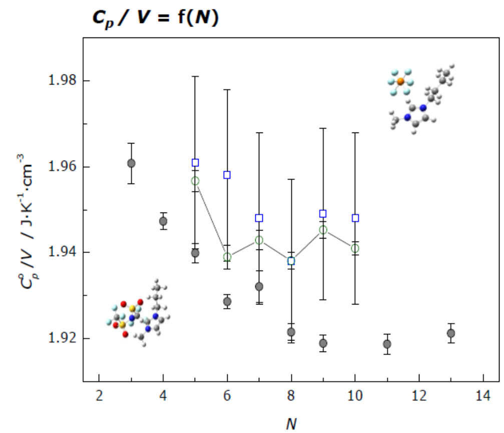
Micro Differential Scanning Calorimetry

Setaram :
Calvet Type Micro DSC III

High Precision heat capacity measurements ..ILs







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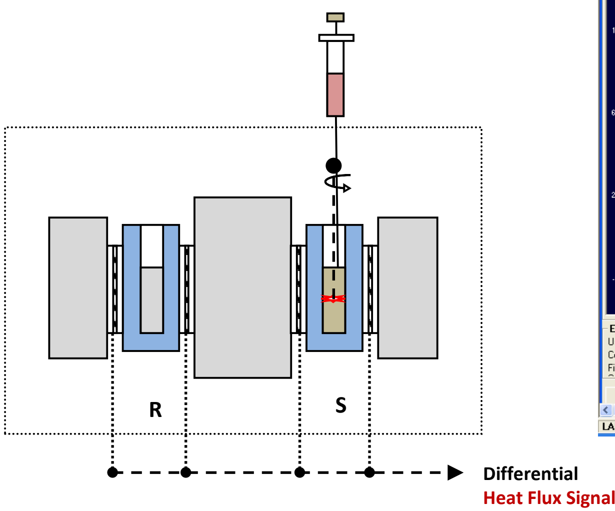
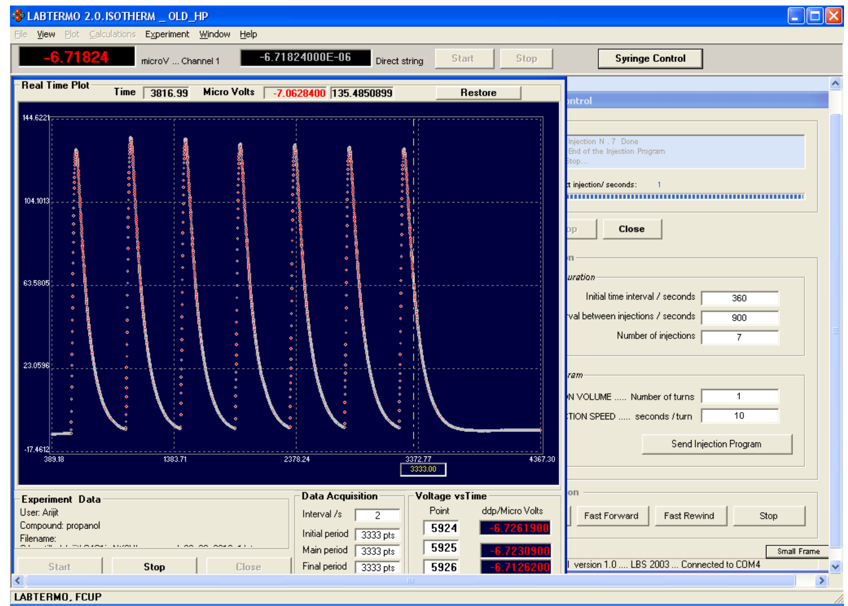
Isothermal Titration Calorimetry

Thermochemistry Laboratory, Lund, Sweden
Twin heat conduction calorimeter





Luís M. N. B. F. Santos et al. *J. Therm. Anal. Calorim.* 2007, 89, 175-180