Trend Shift: The impact of the nanostructure on the behavior of ionic liquids

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http://path.web.ua.pt
http://www.facebook.com/PATh.group

Path (path.web.ua.pt)

http://path.web.ua.pt

ThermPhys

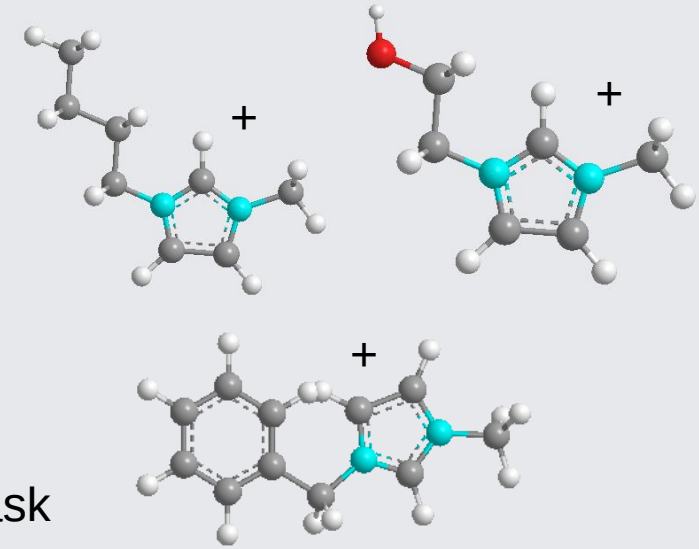
Working Group

Thermophysical Properties of Solids and Fluids

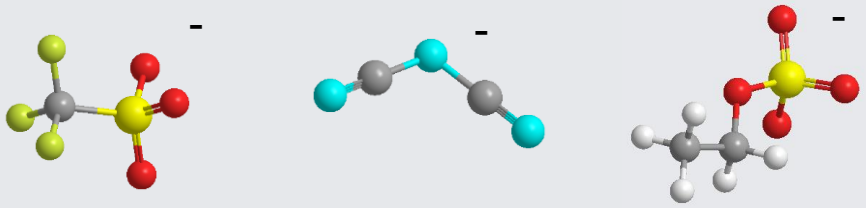
Ionic liquids

Physicochemical properties of Ionic Liquids:

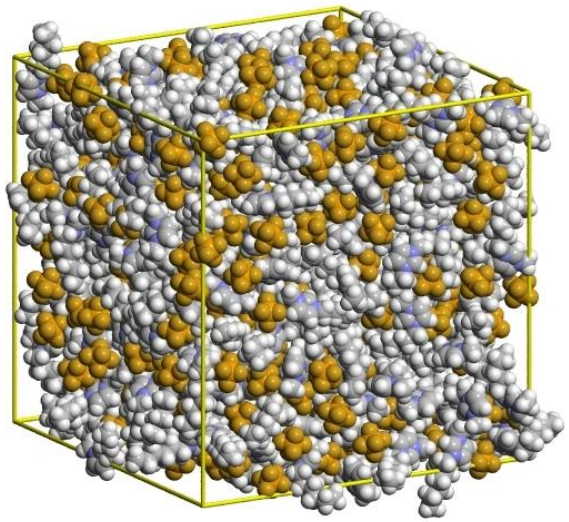
- Low melting temperature (< 100 ºC)
- Large liquidus temperature range
- Negligible vapor pressure
- Non flammable
- High thermal and chemical stability
- Possibility of tune their properties for a specific task

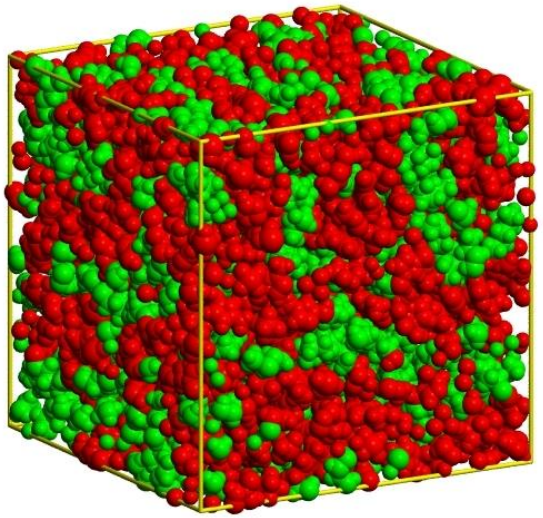


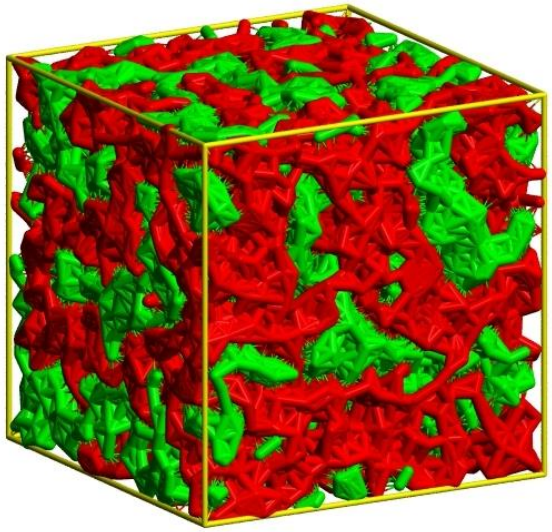
“Designer Solvents”



Nanostructural organization in ionic liquids







A.H. Pádua e J.N.Canongia Lopes, 2006

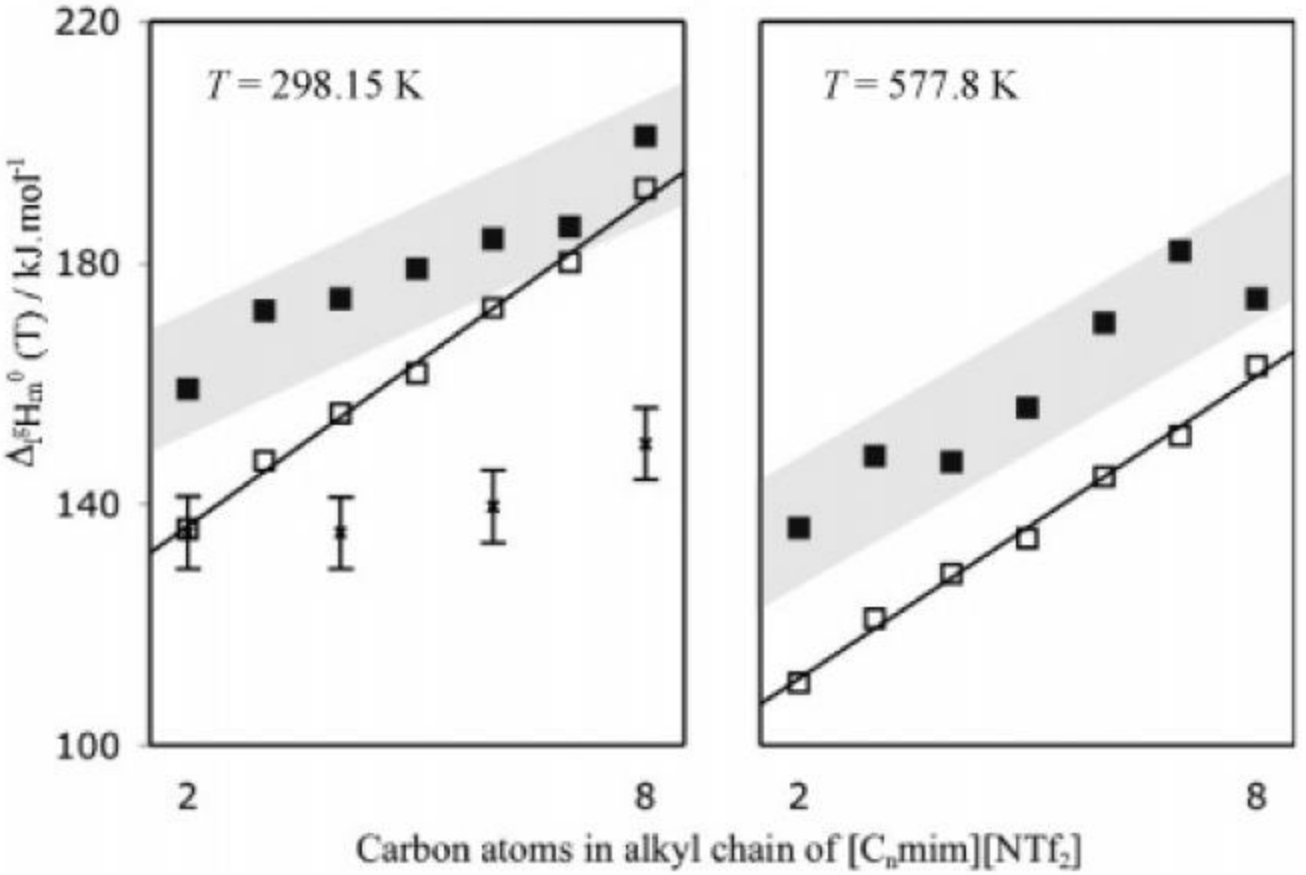
http://oasys2.confex.com/acs/231nm/techprogram/P946950.HTM

Enthalpies of vaporization of ionic liquids

J|A|C|S COMMUNICATIONS

Ionic Liqu

Luís M.
José M. S. S. I
Centro de Investig
4169 007 Porto, Port
Instituto de Tec
2780 901 Oeiras, Por
de Ciências da



PAPER www.rsc.org/pccp | Physical Chemistry Chemical Physics

1-Alkyl-3-methylimid
$[C_nH_{2n+1}mim][C_kH_{2l}$

Marijana Blesic,[ab] Małgorzata
H. Q. Nimal Gunaratne,[a] José
Agílio A. H. Pádua,[c] Kenneth

Received 22nd May 2009, Accepted 1
First published as an Advance Article
DOI: 10.1039/b910177m

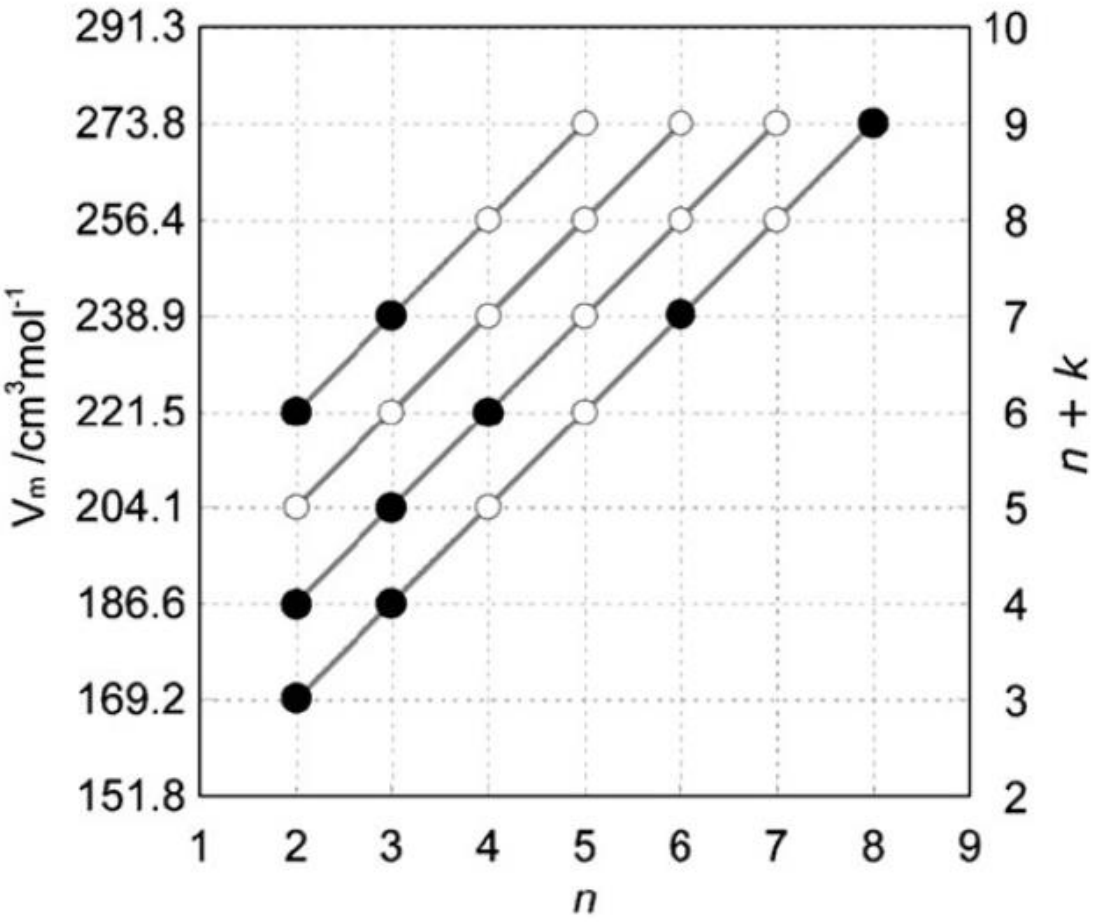


Fig. 7 Experimental molar volume of 1-alkyl-3-methylimidazolium alkylsulfonate, $[C_nmim][C_kSO_3]$, ionic liquids at 333.15 K (●) as a

Group contribution methods

Available online at www.sciencedirect.com
ScienceDirect
Fluid Phase Equilibria 263 (2008) 26–32
FLUID PHASE EQUILIBRIA

ELSEVIER

Available online at www.sciencedirect.com

ELSEVIER

Ind. Eng. Chem. Res. **2008,** *47,* 5751–5757

A Grou

AIChE

Group Contribution Methods for the Prediction of Thermophysical and Transport Properties of Ionic Liquids

Ramesh L. Gardas and João A. P. Coutinho
CICECO, Departamento de Química, Universidade de Aveiro, Aveiro 3810-193, Portugal

DOI 10.1002/aic.11737
Published online April 7, 2009 in Wiley InterScience (www.interscience.wiley.com).

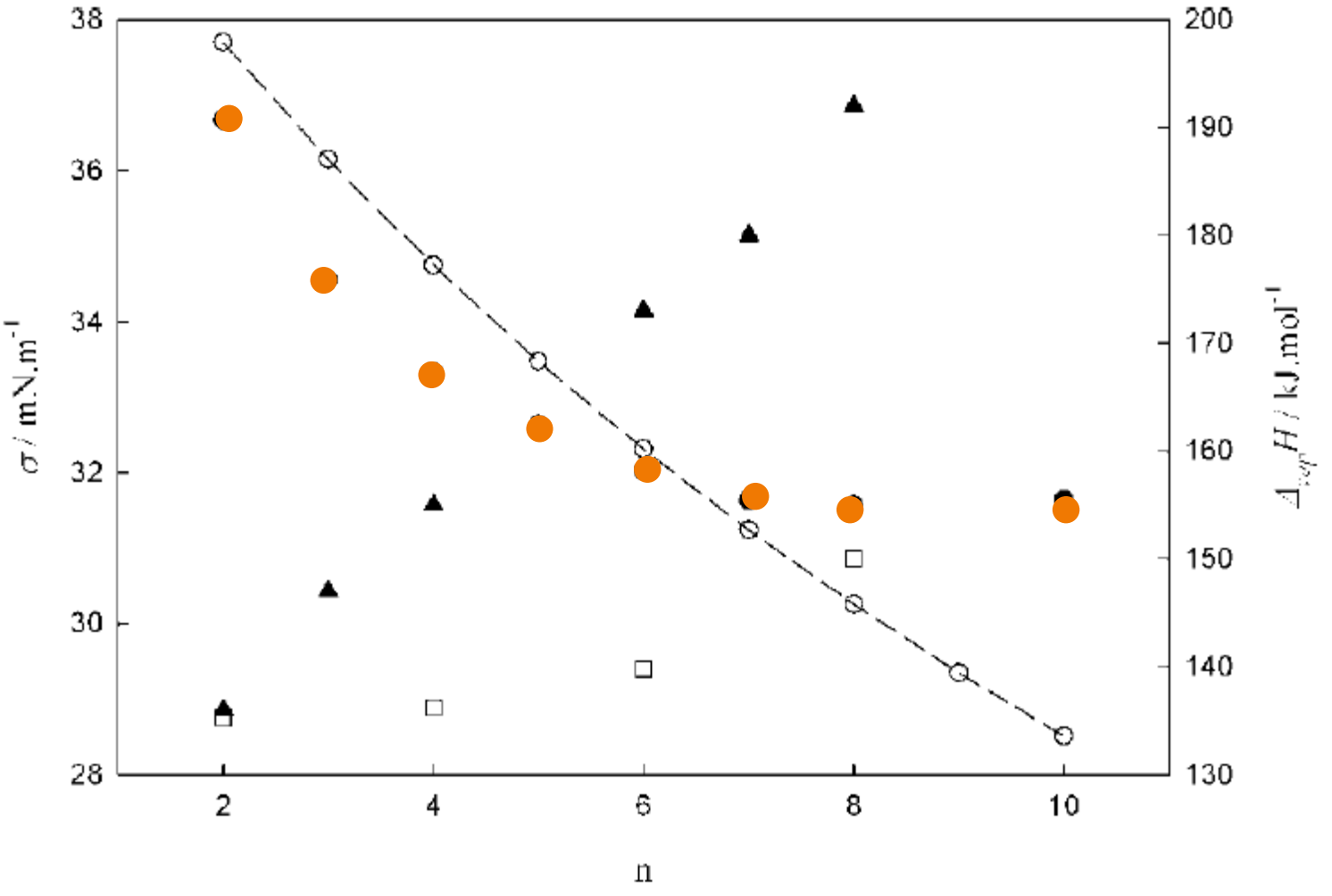
$[C_nC_1im][NTf_2]$ surface tension

1346 *J. Chem. Eng. Data* **2008,** *53,* 1346–1350

Surface T
Bis(trifluo

Pedro J. Carv

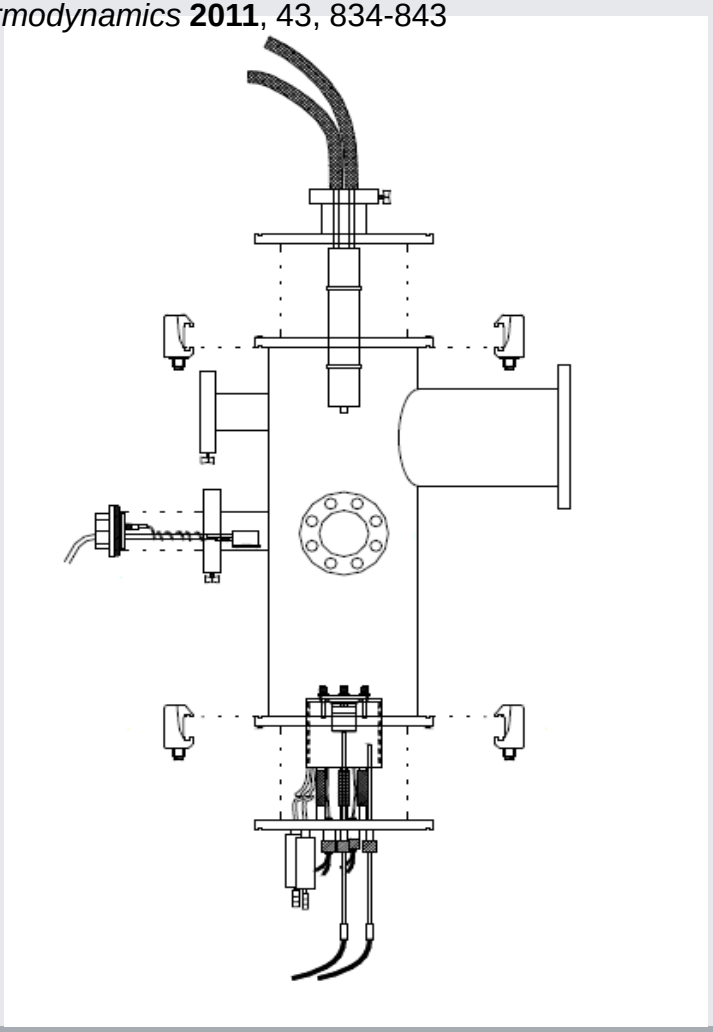
CICECO, Depa
and Reaction E
Frias, 4200-465

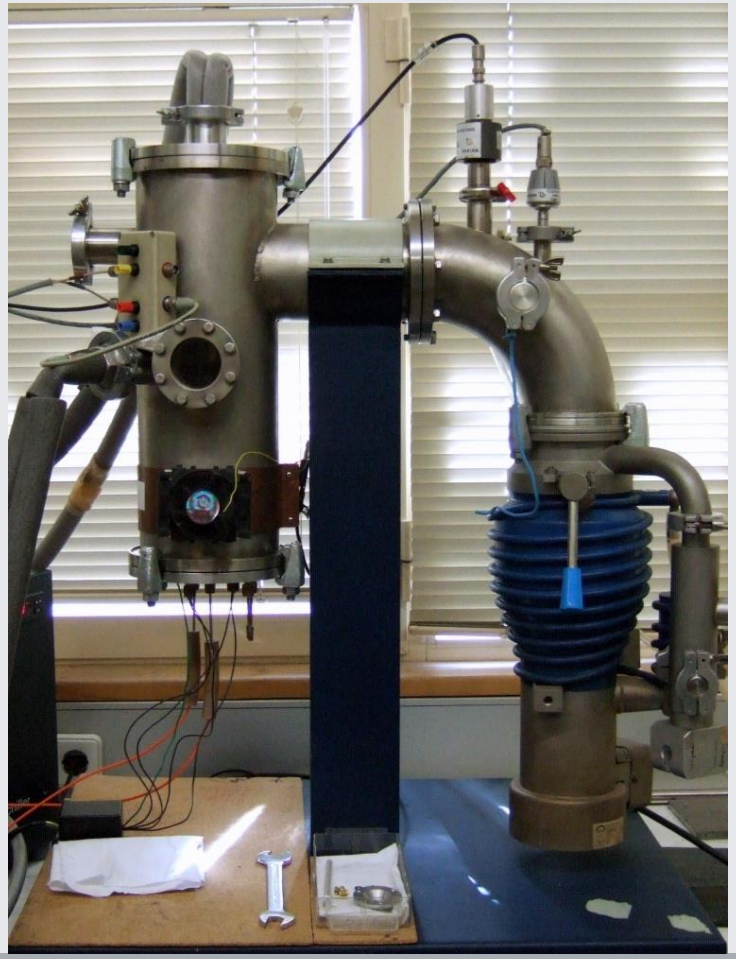


Knudsen Effusion Methods

Knudsen effusion apparatus combined with a quartz crystal microbalance

Santos, L.M.N.B.F.; Lima, L.M.S.S.; Lima, C.F.R.A.C.; Magalhães, F.D.; Torres, M.C.; Schröder, B.; Ribeiro da Silva, M.A.V.
J. Chem. Thermodynamics **2011**, 43, 834-843





THE JOURNAL OF PHYSICAL CHEMISTRY B

ARTICLE

pubs.acs.org/JPCB

High-Accuracy Vapor Pressure Data of the Extended $[C_nC_1im][Ntf_2]$ Ionic Liquid Series: Trend Changes and Structural Shifts

Marisa A. A. Rocha,[†] Carlos F. R. A. C. Lima,[†] Lígia R. Gomes,[§] Bernd Schröder,[‡] João A. P. Coutinho,[‡] Isabel M. Marrucho,[‡,∥] José M. S. S. Esperança,[∥] Luís P. N. Rebelo,[∥] Karina Shimizu,[#] José N. Canongia Lopes,[∥,#] and Luís M. N. B. F. Santos[*,†]

[†]Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, R. Campo Alegre 687, P-4169-007 Porto, Portugal

[‡]CICECO, Departamento de Química, Universidade de Aveiro, P-3810-193 Aveiro, Portugal

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[∥]Instituto de Tecnologia Química e Biológica, ITQB2, Universidade Nova de Lisboa, Av. República, Apartado 127, P-2780-901 Oeiras, Portugal

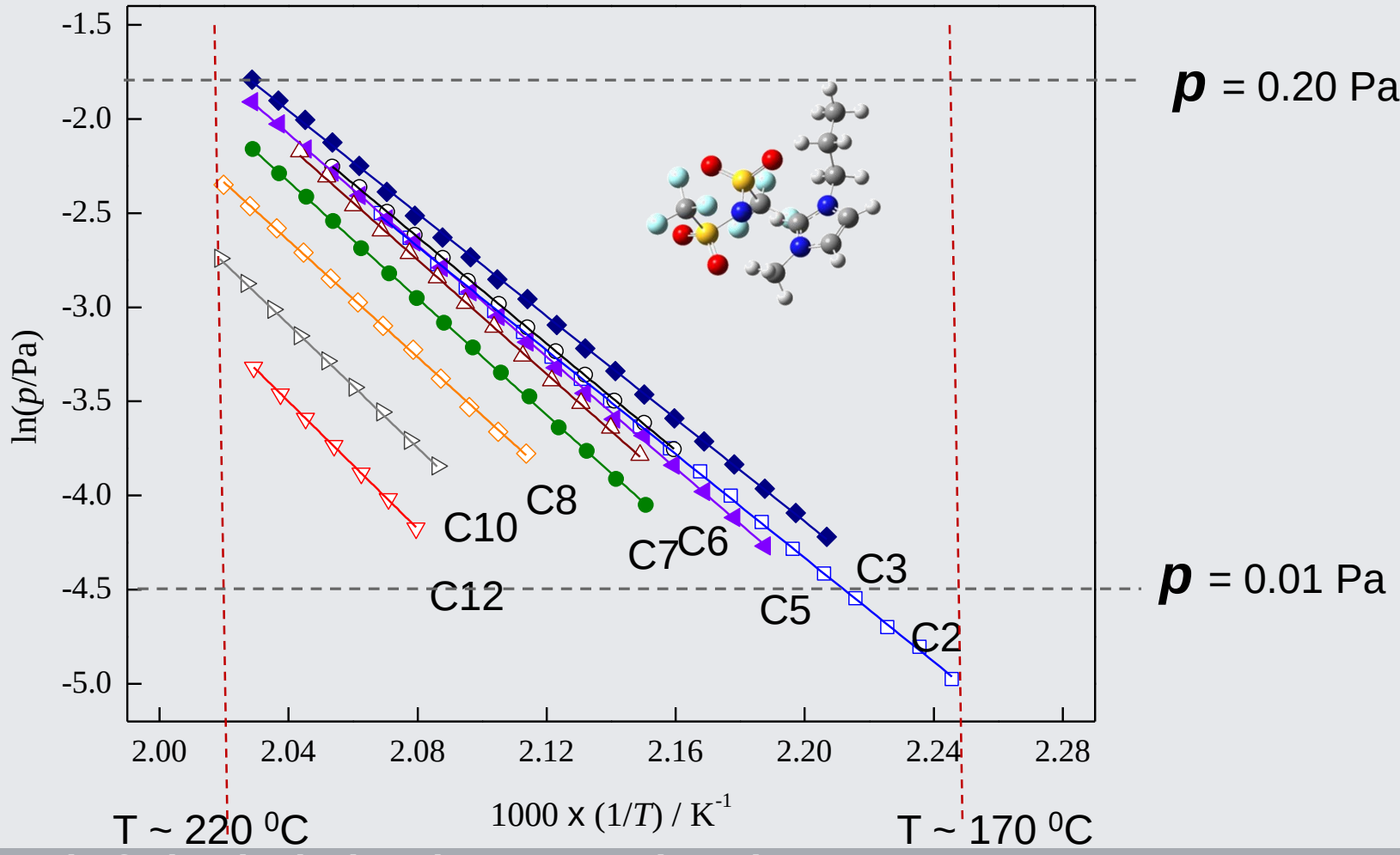
[#]Centro de Química Estrutural/IST, Av. Rovisco Pais, P-1049-001 Lisboa, Portugal

Supporting Information

$[C_nC_1im]$ $[NTf_2]$ volatility

http://path.web.ua.pt

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

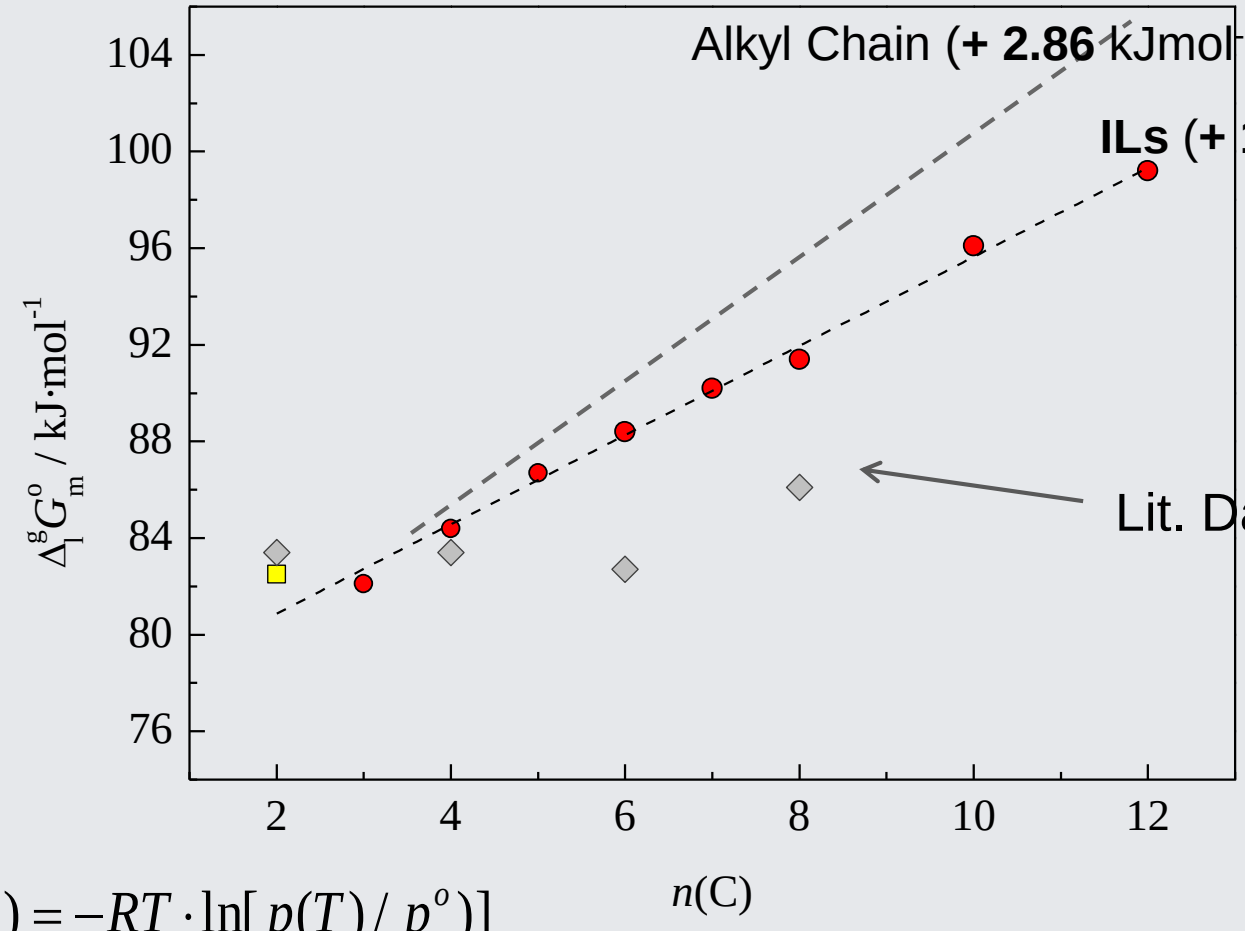


The Journal of Physical Chemistry B 115 (2011) 10919-10926

$[C_nC_1im]$ $[NTf_2]$ volatility

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

(data corrected to 298.15 K)



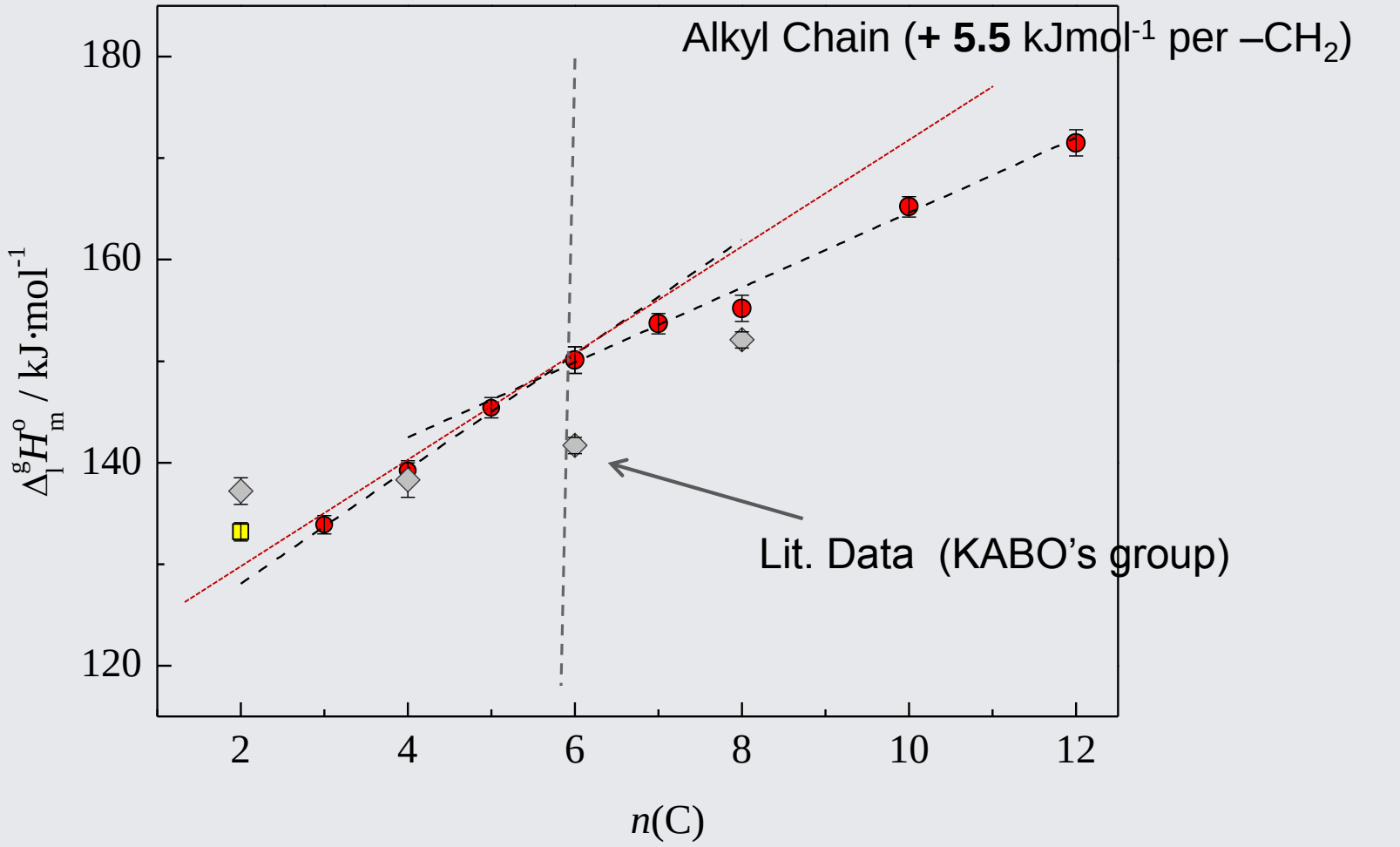
$$\Delta_l^g G_m^o(T) = -RT \cdot \ln[p(T)/p^o)]$$

$[C_nC_1im]$ $[NTf_2]$ volatility

http://path.web.ua.pt

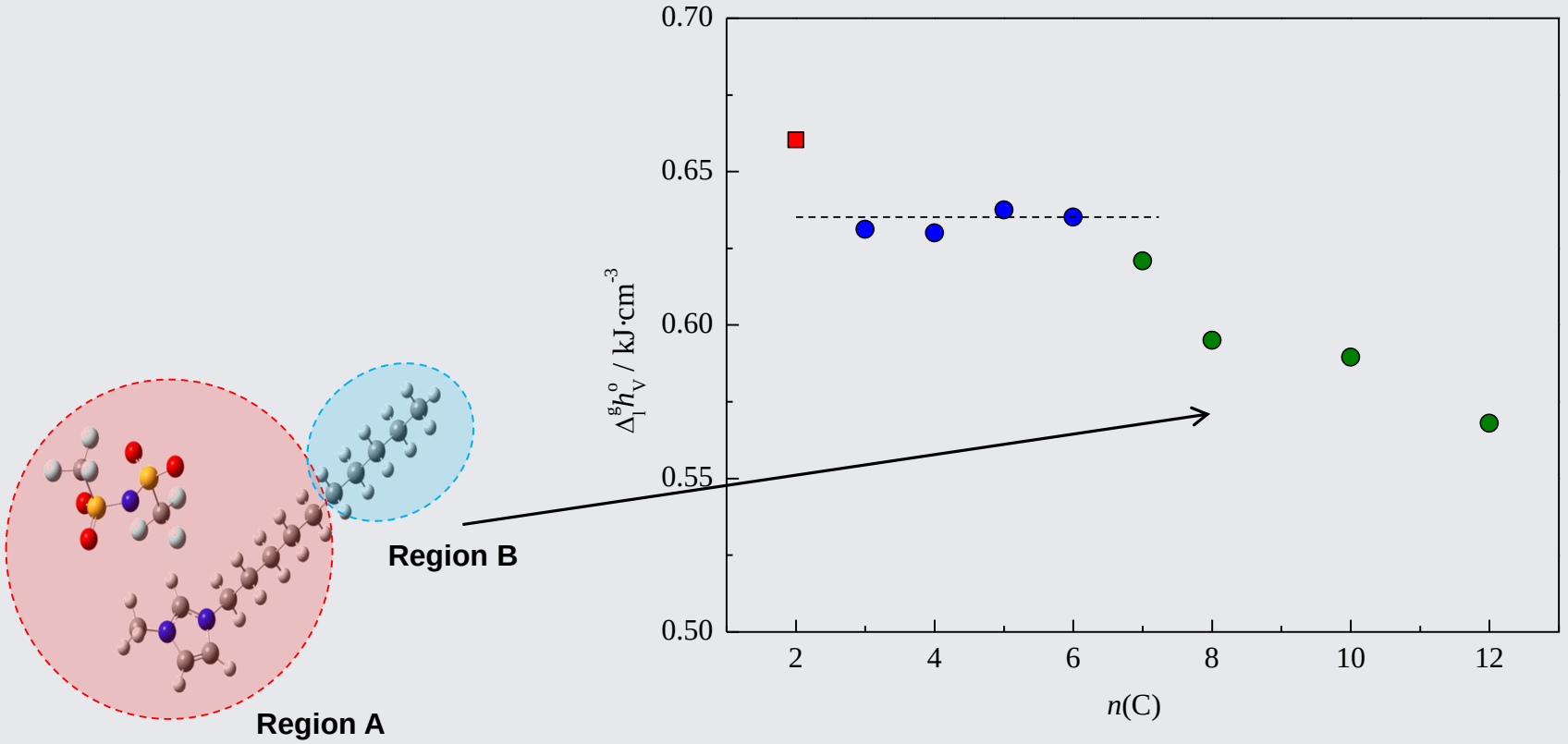
Volatility Study of $[C_nC1im][NTf_2]$ (n = 2 – 12)…

(data corrected to 298.15 K)



$[C_nC_1im][NTf_2]$ volatility

VOLUMIC ENTHALPY OF VAPORIZATION



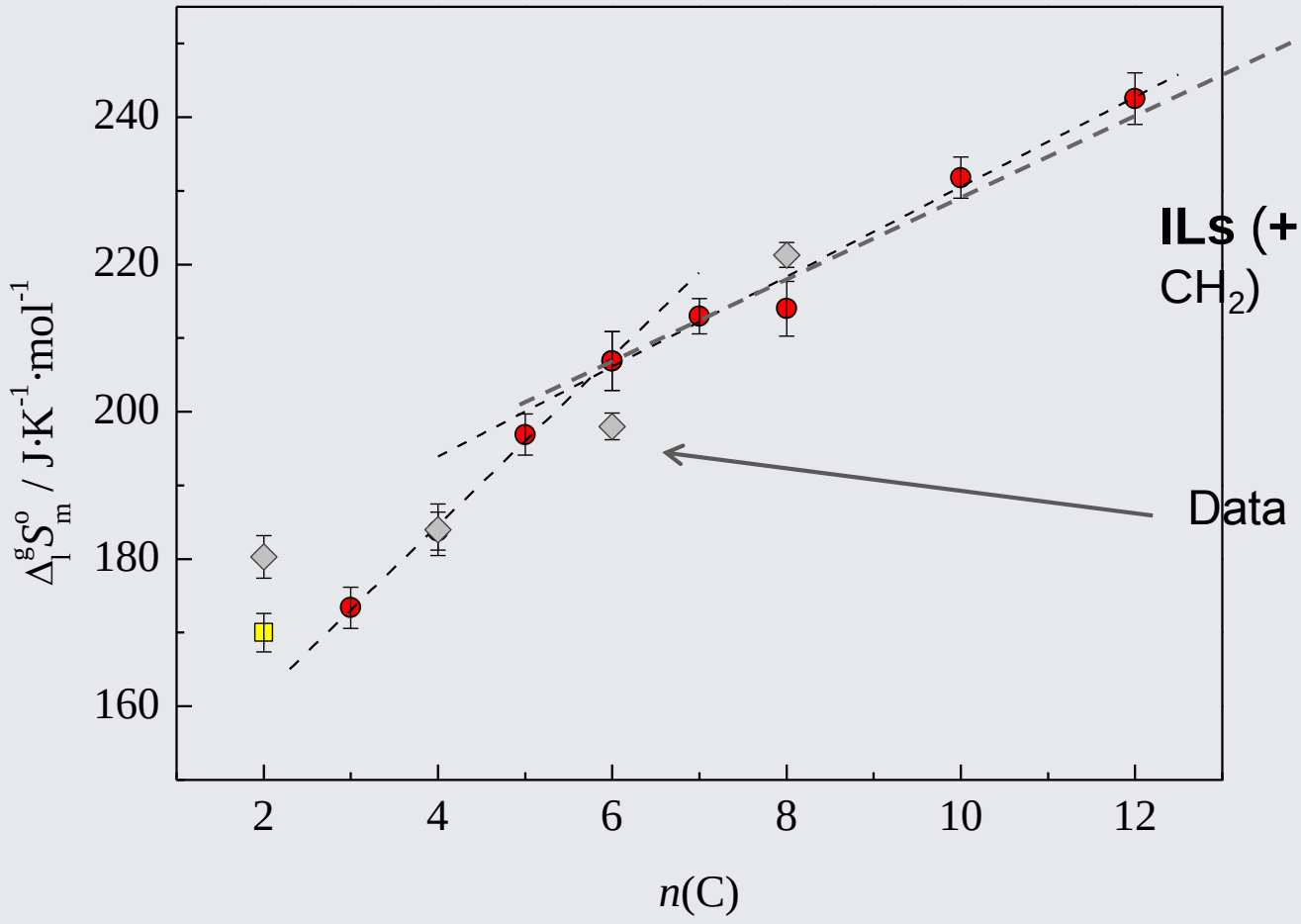
$[C_nC_1im]$ $[NTf_2]$ volatility

http://path.web.ua.pt

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

(data corrected to 298.15 K)

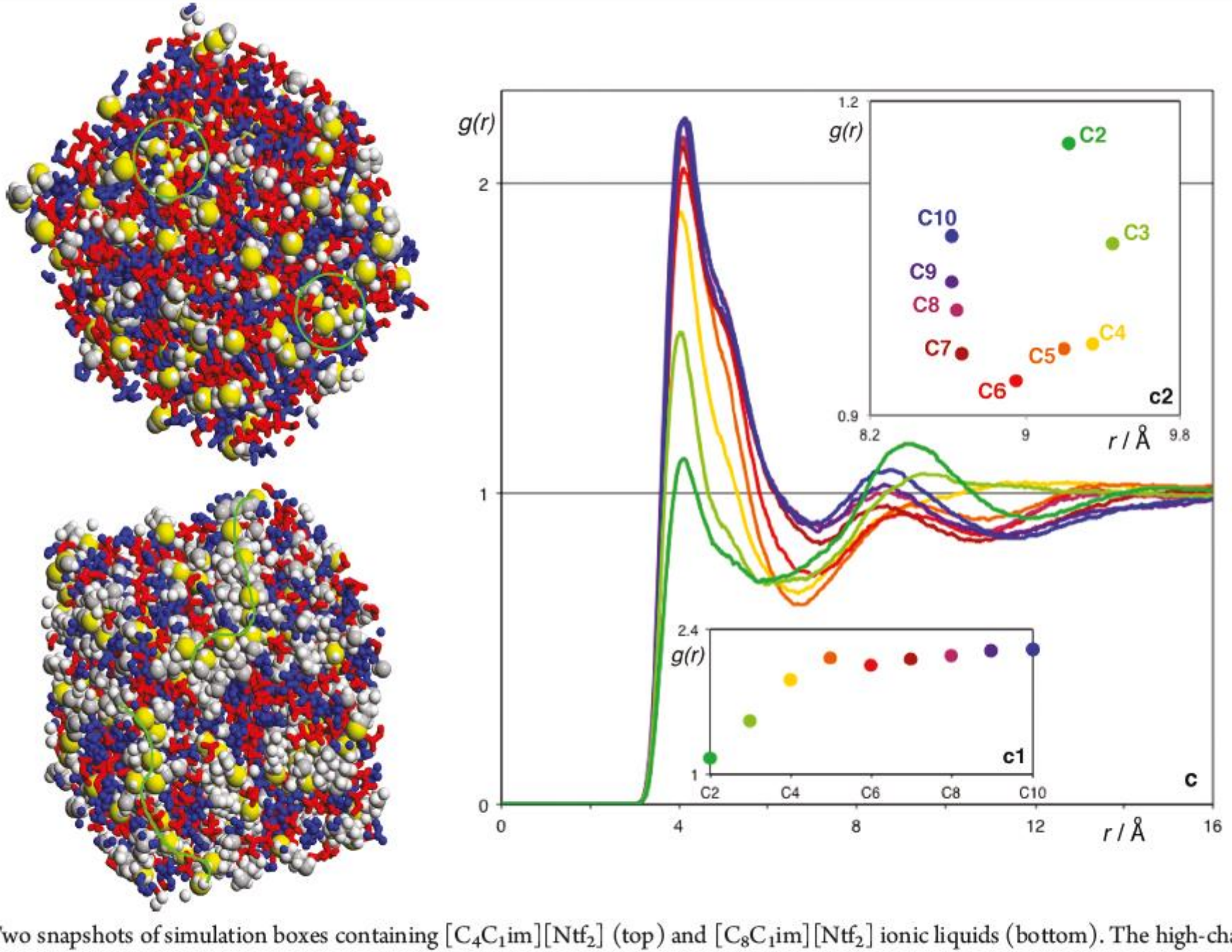
Alkyl Chain (**+ 6.1** $J.K^{-1}mol^{-1}$ per $–CH_2$)



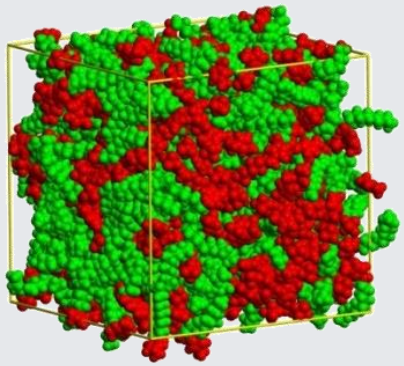
ILs (**+ 7.0** $J.K^{-1}mol^{-1}$ per $–CH_2$)

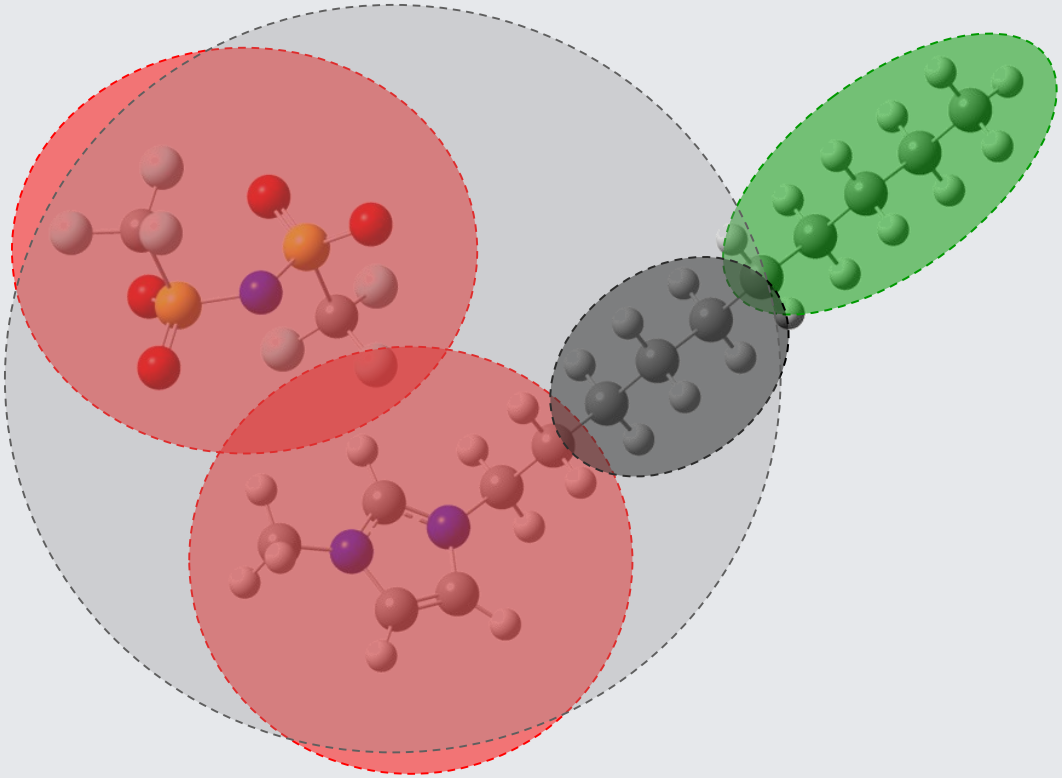
Data (KABO's group)

The Journal of Physical Chemistry B 115 (2011) 10919-10926



re 6. Two snapshots of simulation boxes containing $[C_4C_1im][Ntf_2]$ (top) and $[C_8C_1im][Ntf_2]$ ionic liquids (bottom). The high-charge
ons of the cations and anions are colored as blue and red sticks to highlight the continuity of the polar network. The alkyl side chains (fr
ard) are colored using space-filled atoms and the SPK convention (carbon, gray; hydrogen, white). The terminal atoms (CT) of each alkyl sid

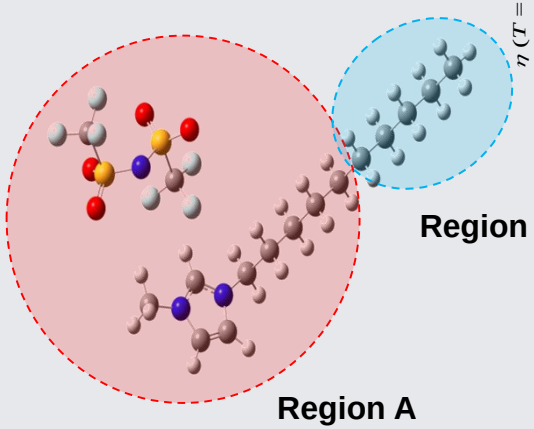




$[C_nC_1im][NTf_2]$ viscosity

Vogel–Fulcher–Tamman (VFT)… $\eta = A \cdot \exp[B/(T - Tg)]$

Viscosity Data
(Tariq et al. 2010)



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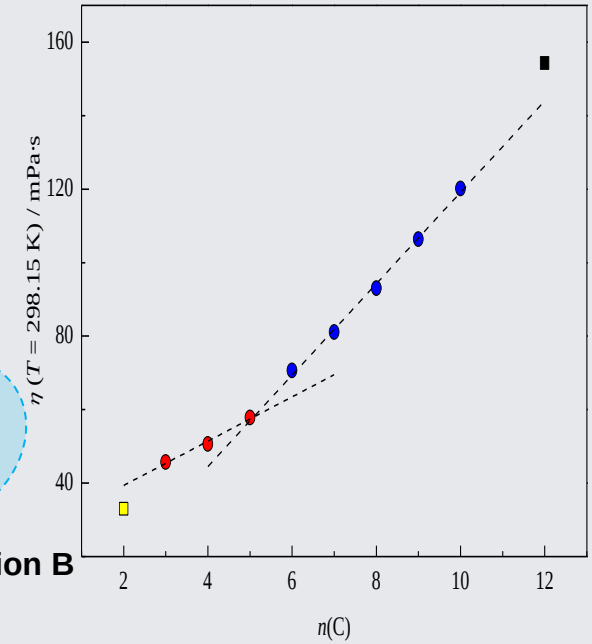
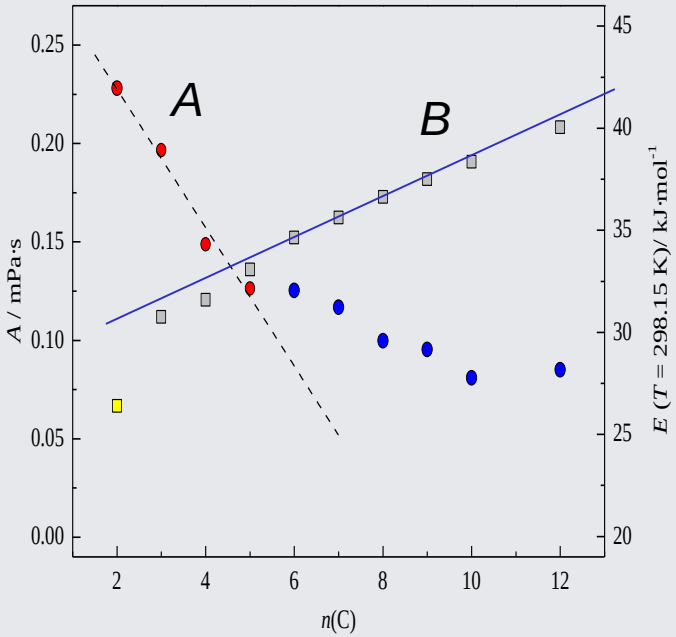




Ionic liquids heat capacity

Ind. Eng. Chem. Res. **2008,** *47,* 5751–5757

A Group Contribution Method for Heat Capacity Estimation of Ionic Liquids

Ramesh L. Gardas* and João A. P. Coutinho*

$$C_{pL}^{\exp}\ (\mathrm{J\ mol^{-1}K^{-1}}) = (1.9516 \pm 0.0090)\ \mathrm{V/cm^3\ mol^{-1}} \quad (R^2 = 0.9935, \text{ at a } 95\% \text{ level of confidence}) \quad (6)$$

Heat Capacity of Room-Temperature Ionic Liquids: A Critical Review

Yauheni U. Paulechka[a)]

Chemistry Faculty, Belarusian State University, Leningradskaya 14, 220030 Minsk, Belarus

(Received 11 May 2010; accepted 21 June 2010; published online 27 September 2010)

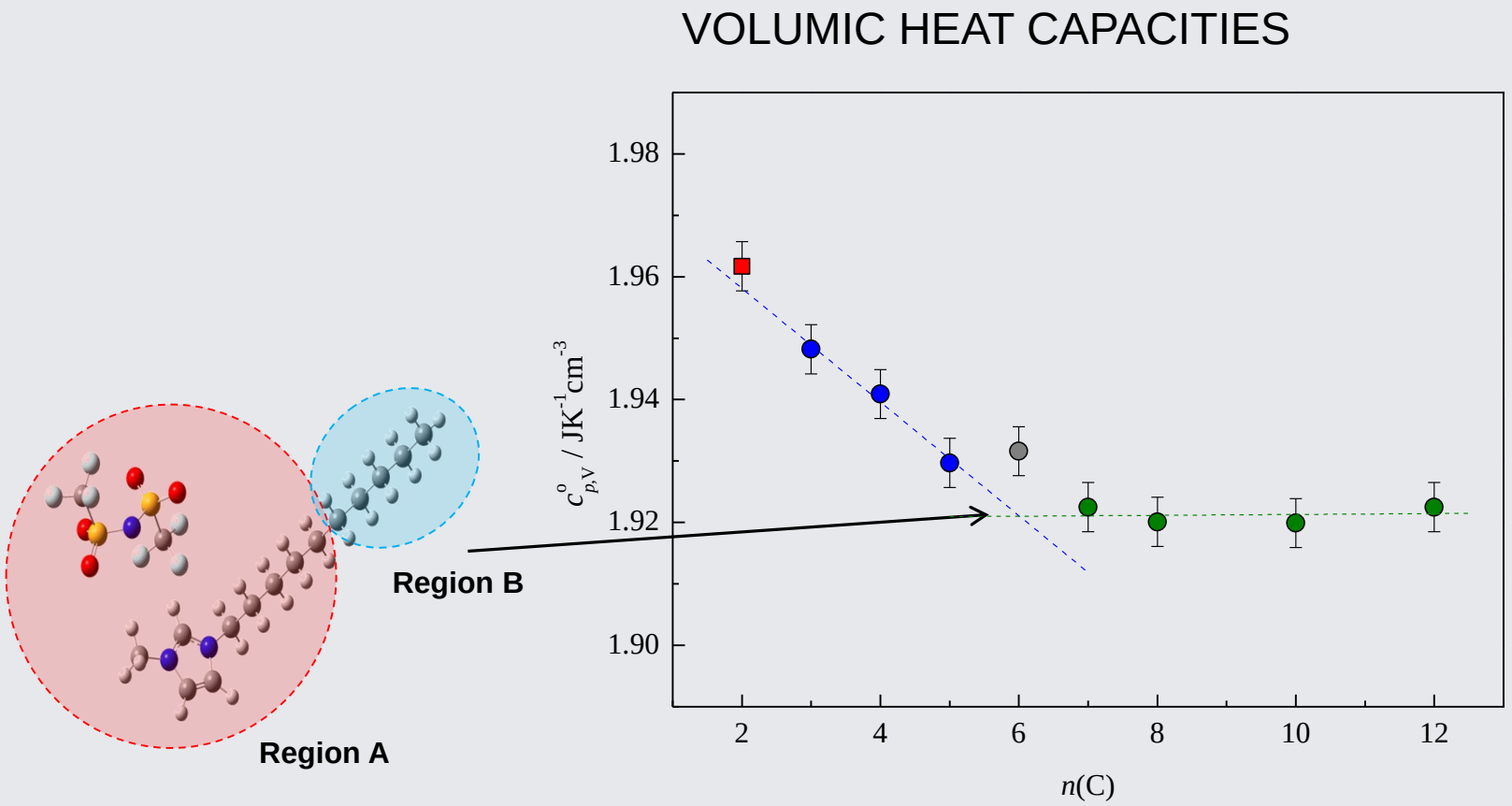
$$(C_p/V)/\mathrm{J\ K^{-1}\ mol^{-1}} = 1.951 + 8.33 \times 10^{-4}(T/\mathrm{K}),$$

$[C_nC_1im][NTf_2]$ heat capacity

http://path.web.ua.pt

High Precision Cp DROP CALORIMETER

Santos, L. M. N. B. F.; Rocha, M. A. A.; Rodrigues, A. S. M. C.; Štejfa, V.; Fulem, M.; Bastos, M.
J. Chem. Themodyn. 2011, **43**, 1818-1823.



$[C_nC_1im]$ $[NTf_2]$ heat capacity

J. Chem. Thermodynamics 53 (2012) 140–143

Contents lists available at SciVerse ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Heat capacities at 298.15 K of the extended $[C_nC_1im][Ntf_2]$ ionic liquid series

Marisa A.A. Rocha [a,*], Margarida Bastos [a], João A.P. Coutinho [b], Luís M.N.B.F. Santos [a,*]

[a] Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal
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Keywords:
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Drop calorimeter
Bis(triflamide)
Ionic liquids

ABSTRACT

High-precision heat capacities at 298.15 K of the $[C_nC_1im][Ntf_2]$ ionic liquid series were measured with an uncertainty of less than ±0.3%, using a drop heat capacity apparatus that was recently updated. The dependence of the c_p^o values on the alkyl side chain length for the extended ionic liquid series $[C_nC_1im][Ntf_2]$ (with $n = 2$ to 8, 10, and 12) displays a trend shift at $[C_6C_1im][Ntf_2]$, which is taken as an evidence for percolation limit. Above this limit there is an increase in the methylene group contribution to the molar heat capacity which is in agreement with the higher molar absolute entropies change observed from the (liquid + vapor) equilibrium results. The obtained experimental results support the model that the ionic liquids tend to be segregated into a polar network and non-polar domains, being followed by an increase of the entropy contribution of the non-polar domains.

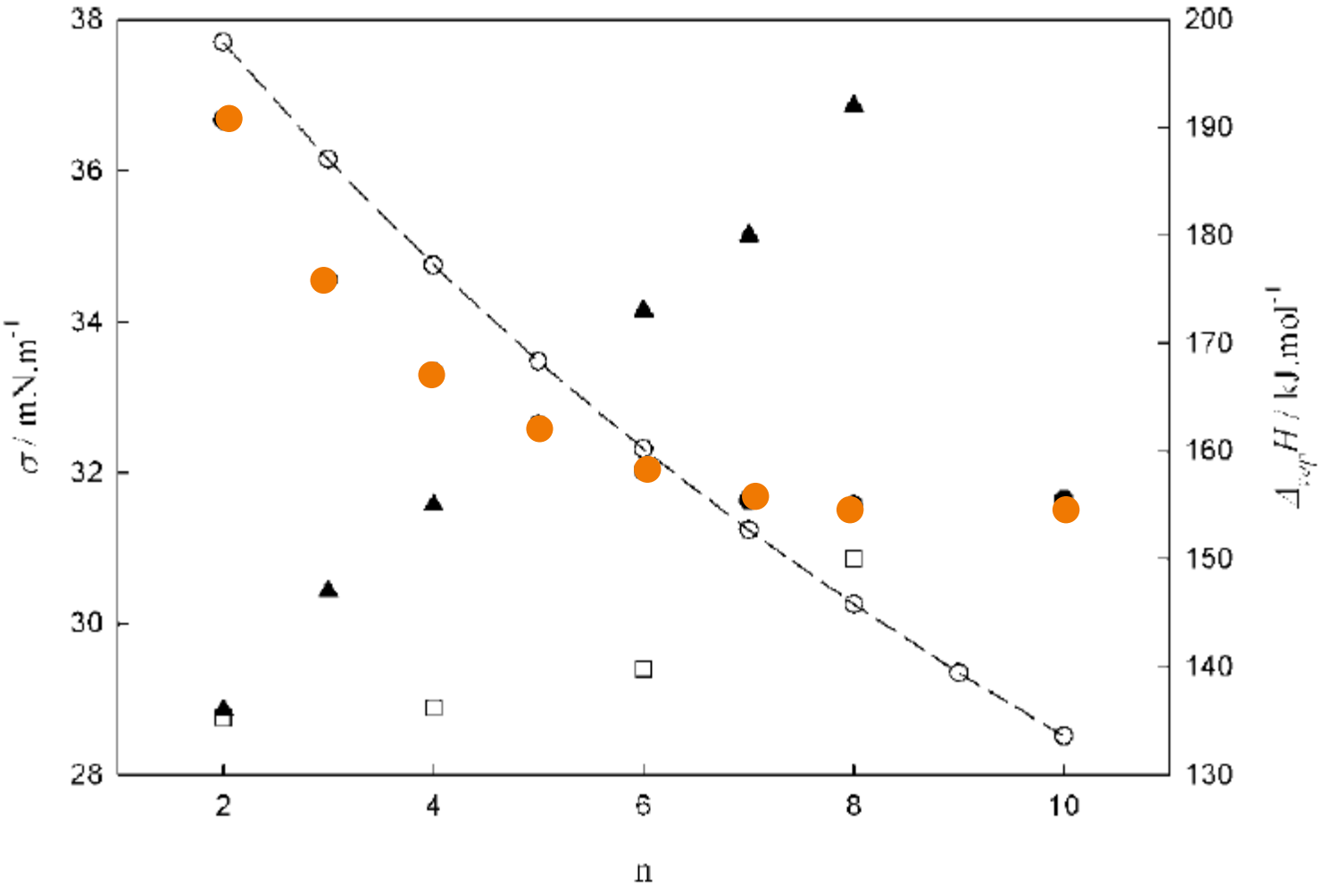
$[C_nC_1im][NTf_2]$ surface tension

1346 *J. Chem. Eng. Data* **2008,** *53,* 1346–1350

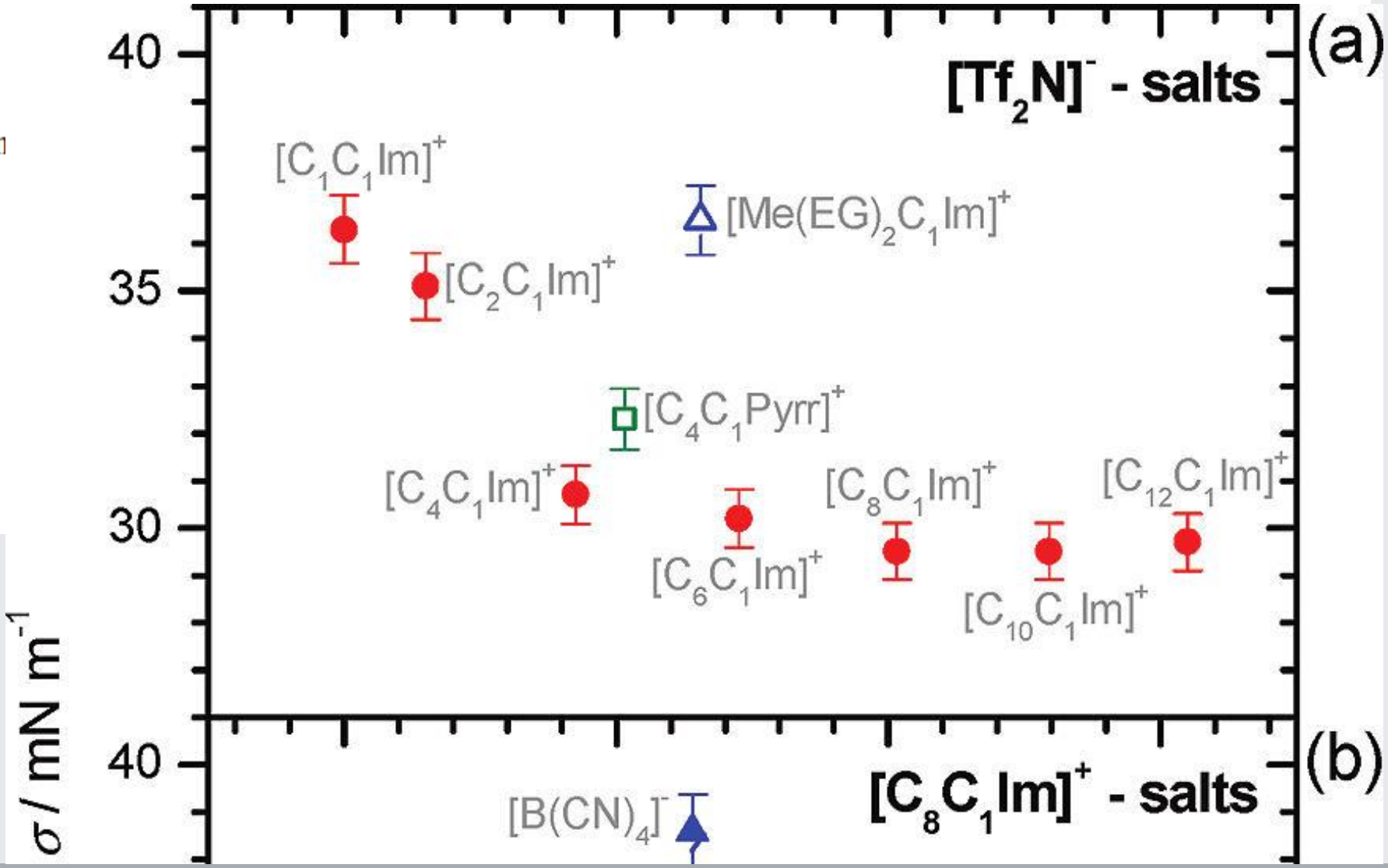
Surface T
Bis(trifluo

Pedro J. Carv

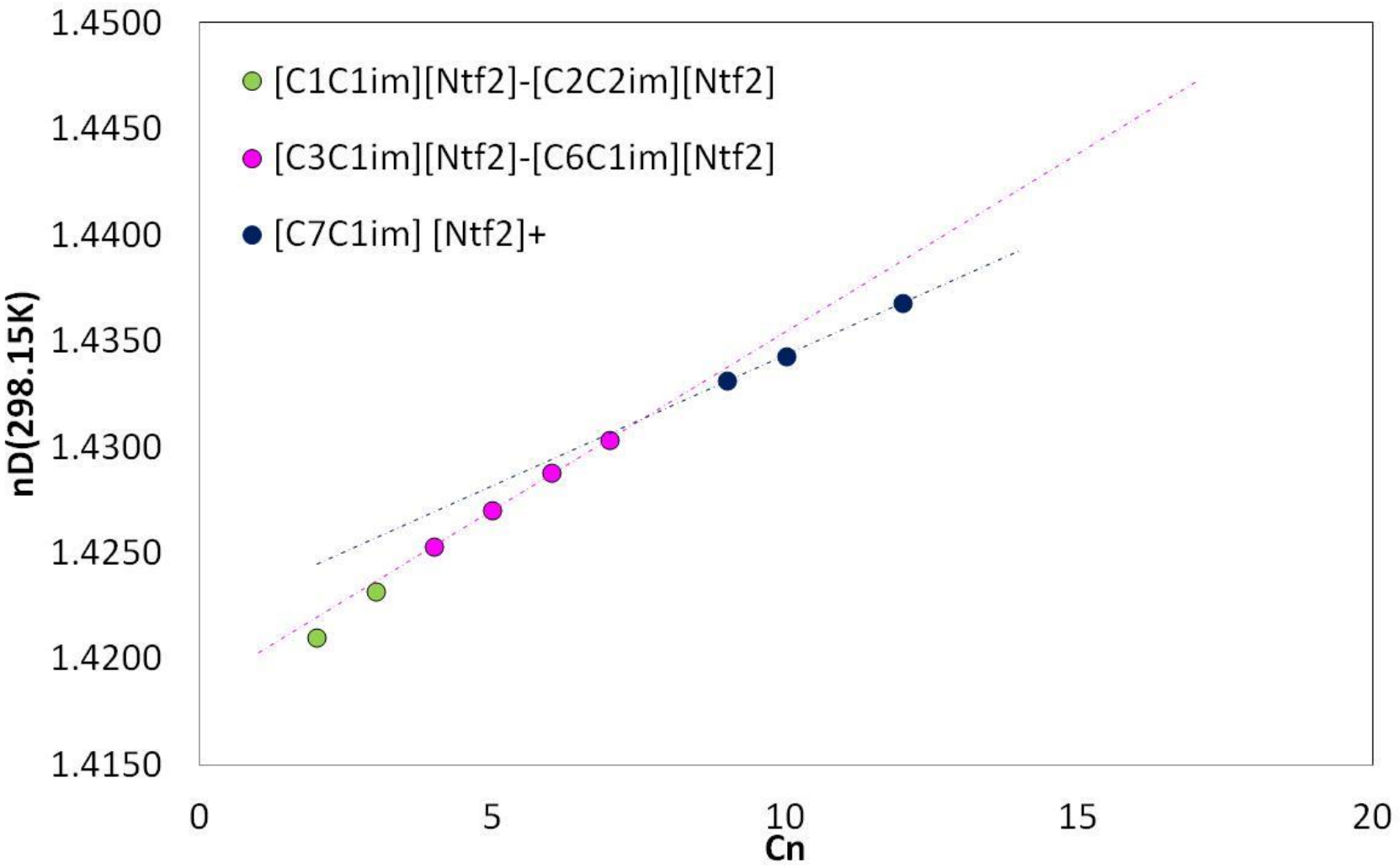
CICECO, Depa
and Reaction E
Frias, 4200-465



$[C_nC_1im][NTf_2]$ surface tension



$[C_nC_1im]$ $[NTf_2]$ refraction index

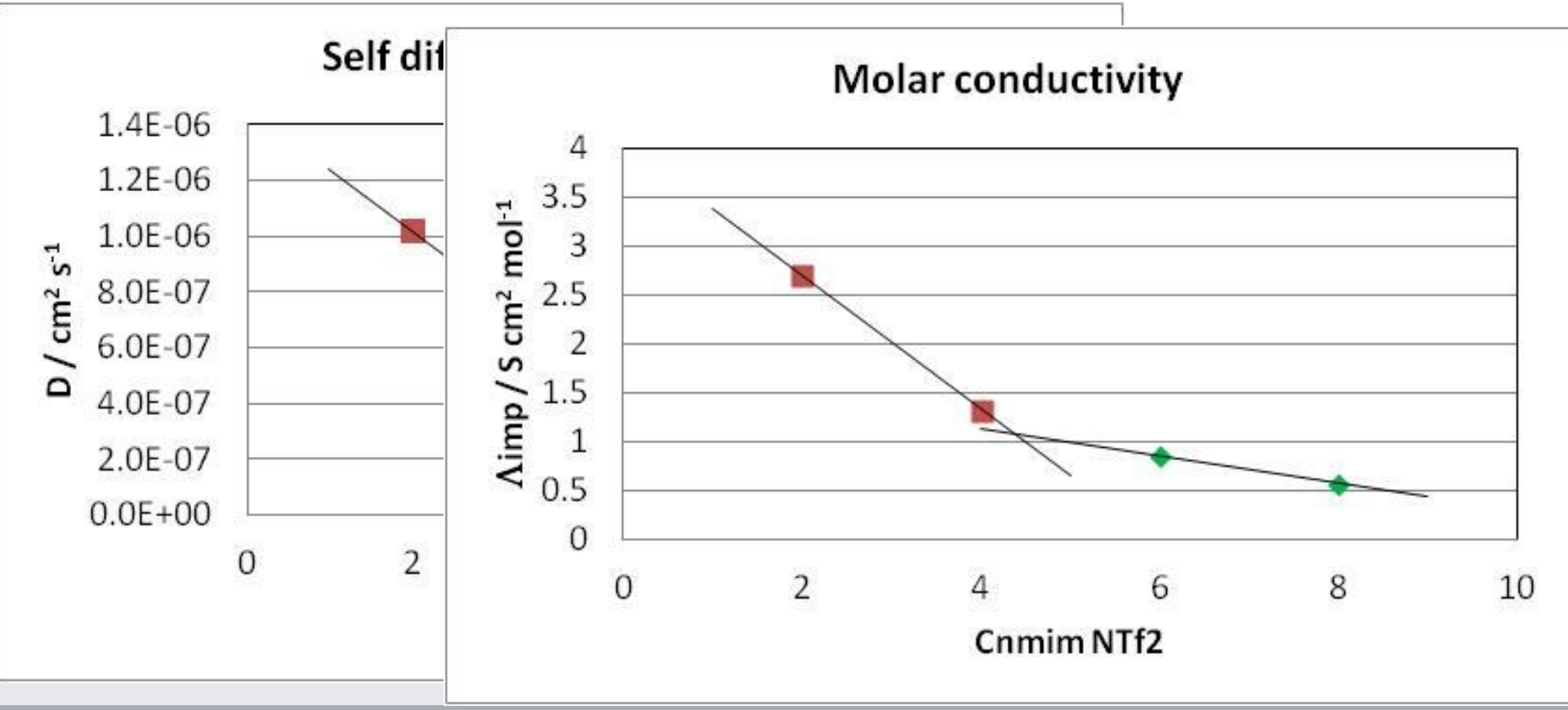


Rocha et al. Unpublished data

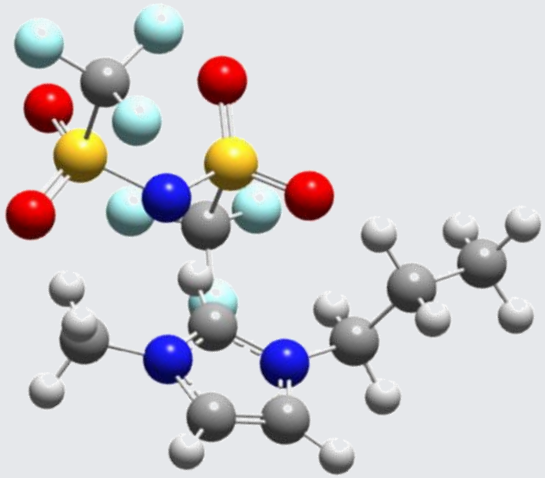
Other thermophysical properties

J. Phys. Chem. B **2005,** *109,* 6103−6110

Physicochemical Properties and Structures of Room Temperature Ionic Liquids. 2. Variation of Alkyl Chain Length in Imidazolium Cation



Symmetric & Asymmetric ILs

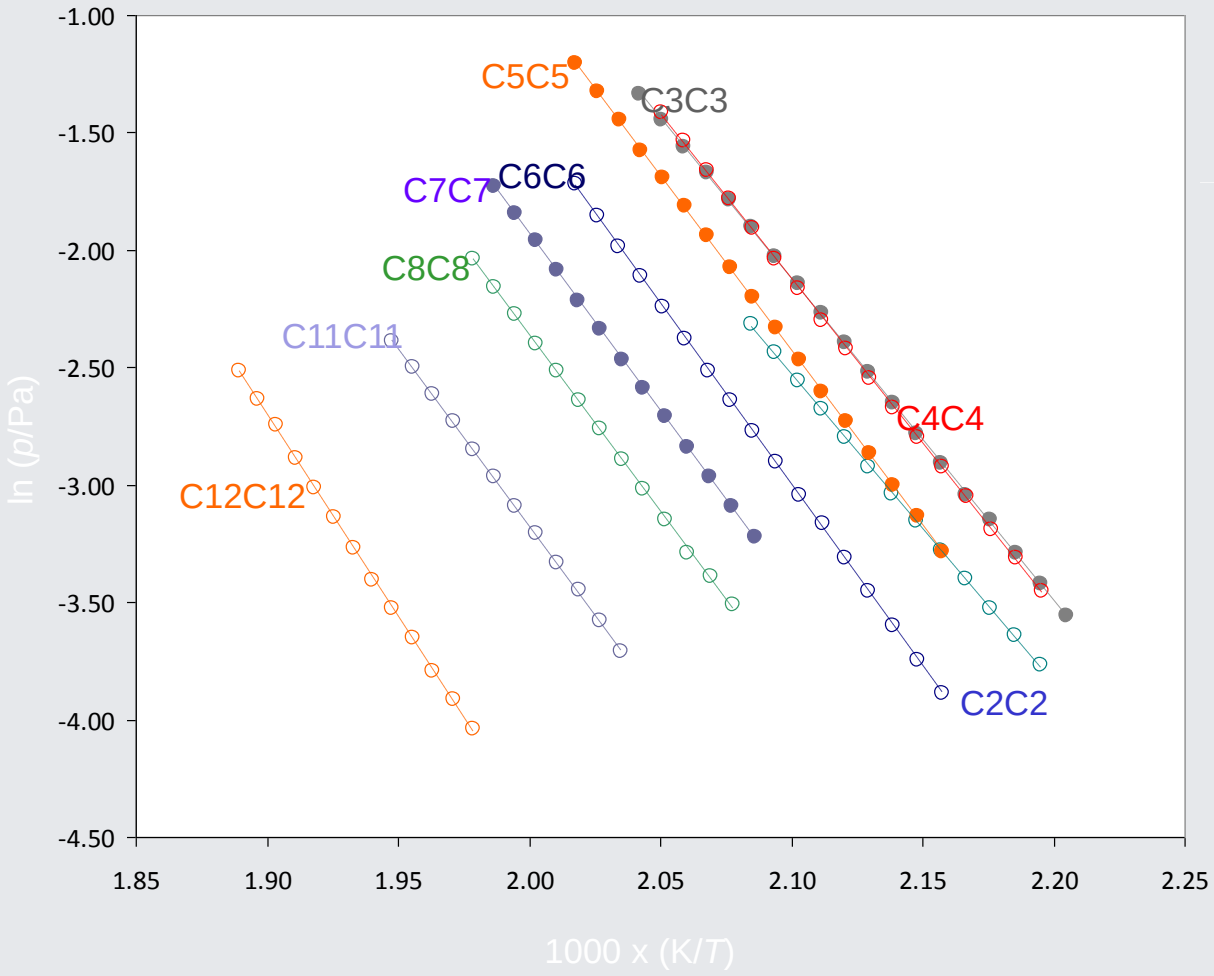


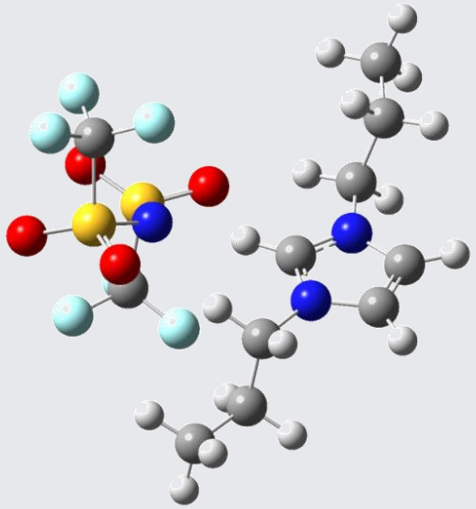
$[C_{N-1}C_1im][NTf_2]$

$[C_{N/2}C_{N/2}im][NTf_2]$

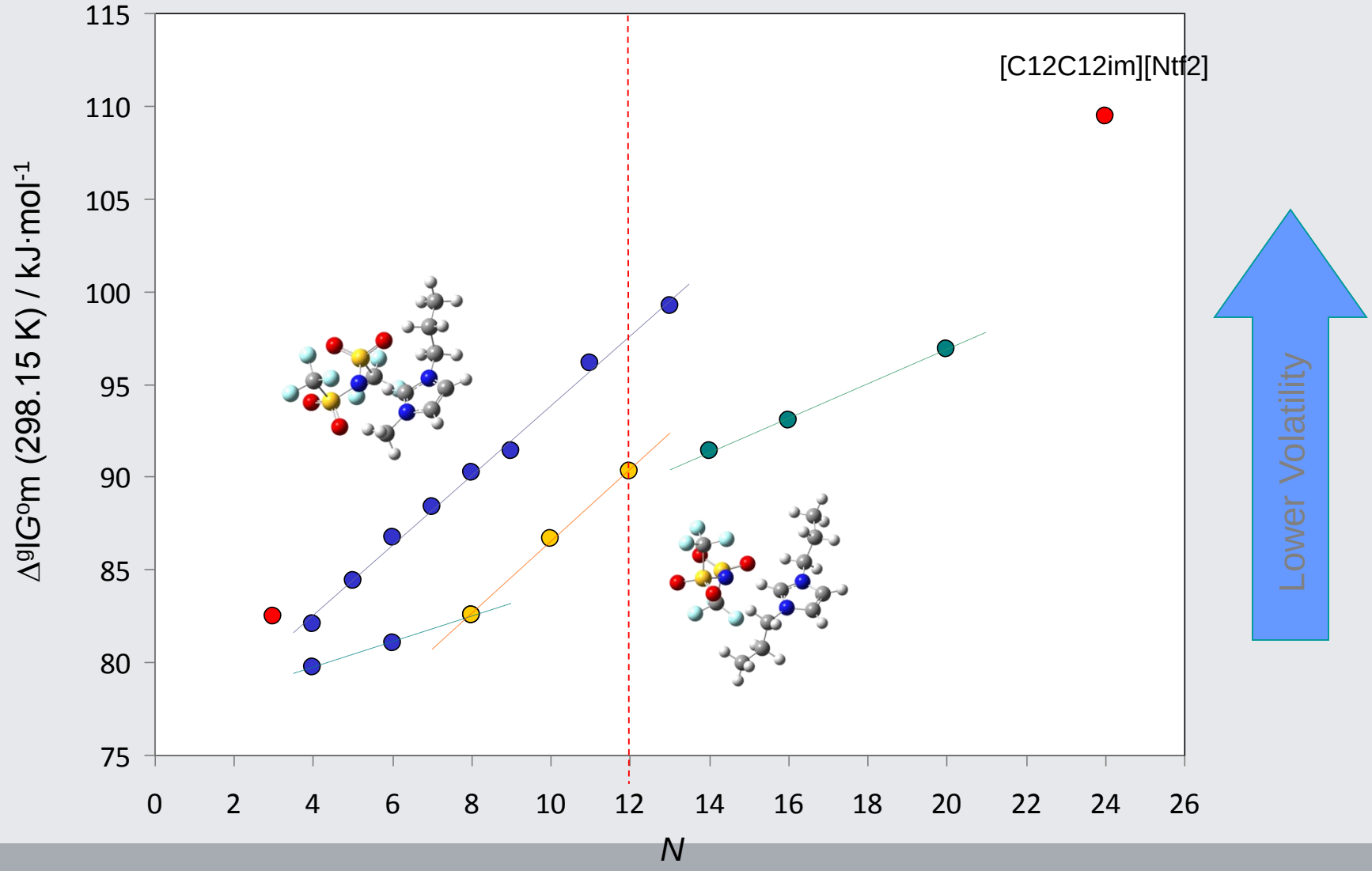
$[C_nC_nim]$ $[NTf_2]$ volatility

M. A. A. Rocha et al. ***J. Phys. Chem. B***, 2012, in press

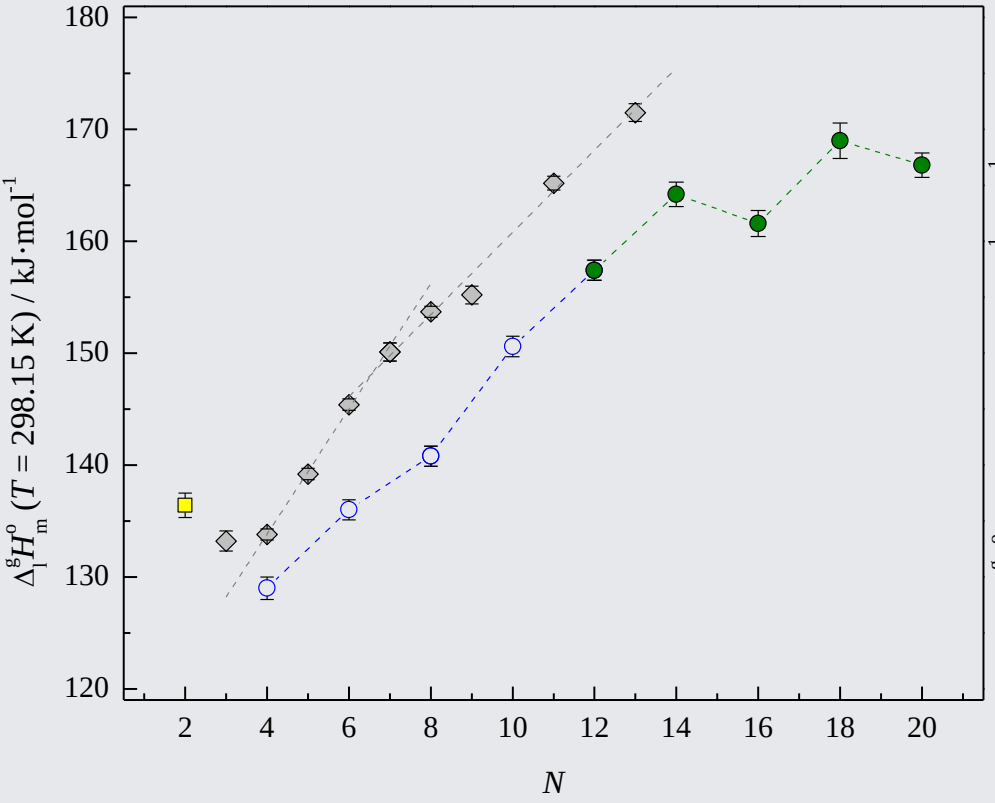


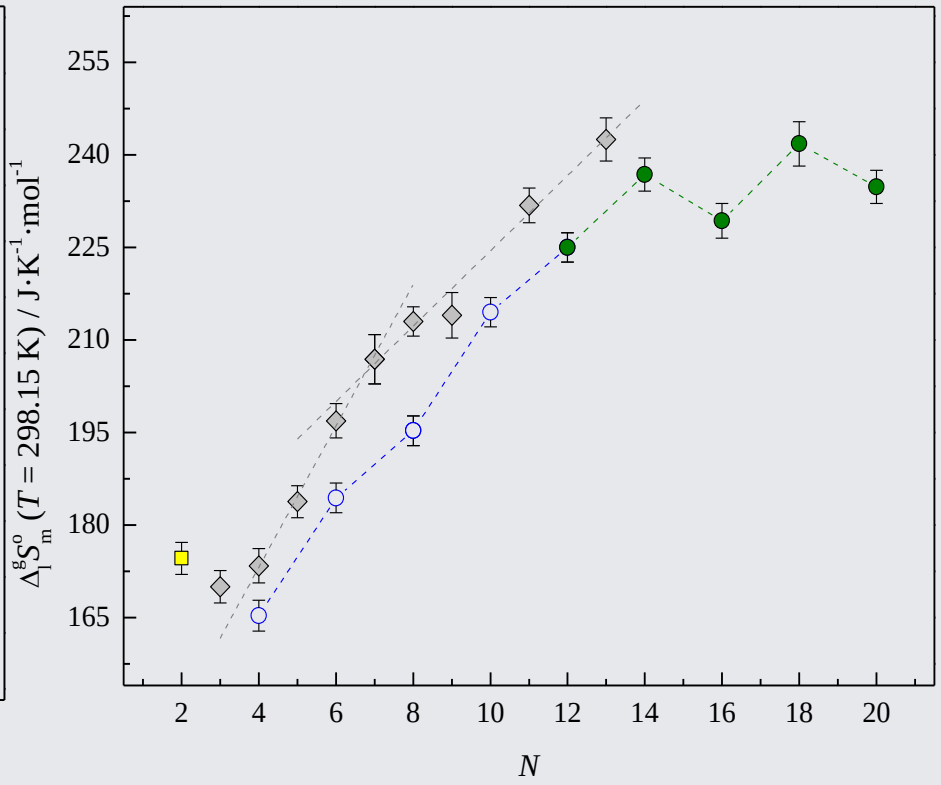


$[C_nC_nim]$ $[NTf_2]$ volatility

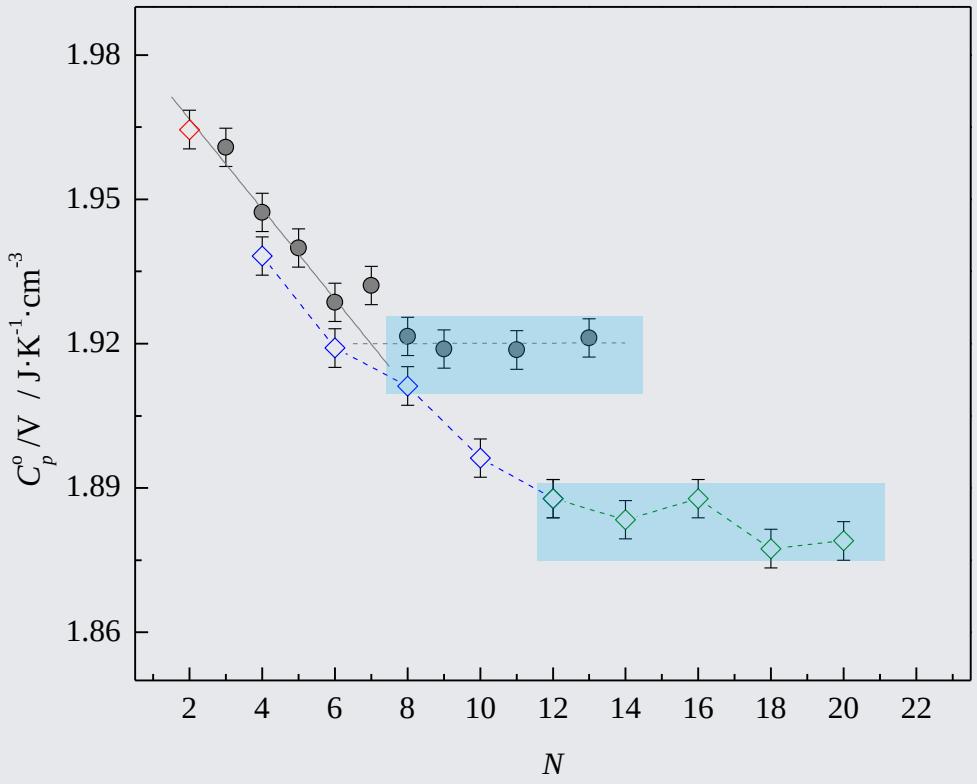


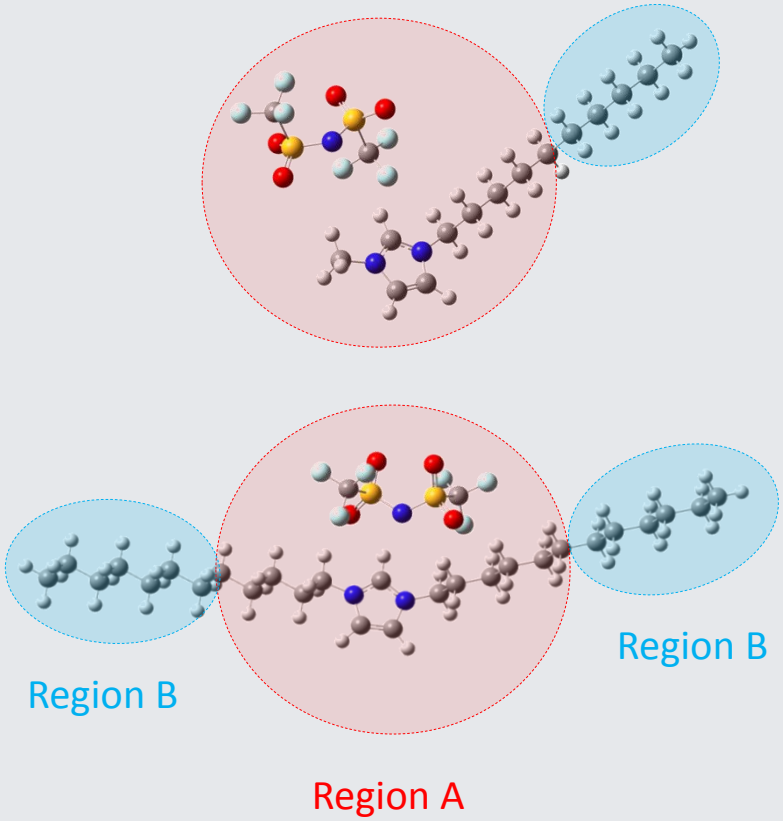
$[C_nC_nim][NTf_2]$ volatility



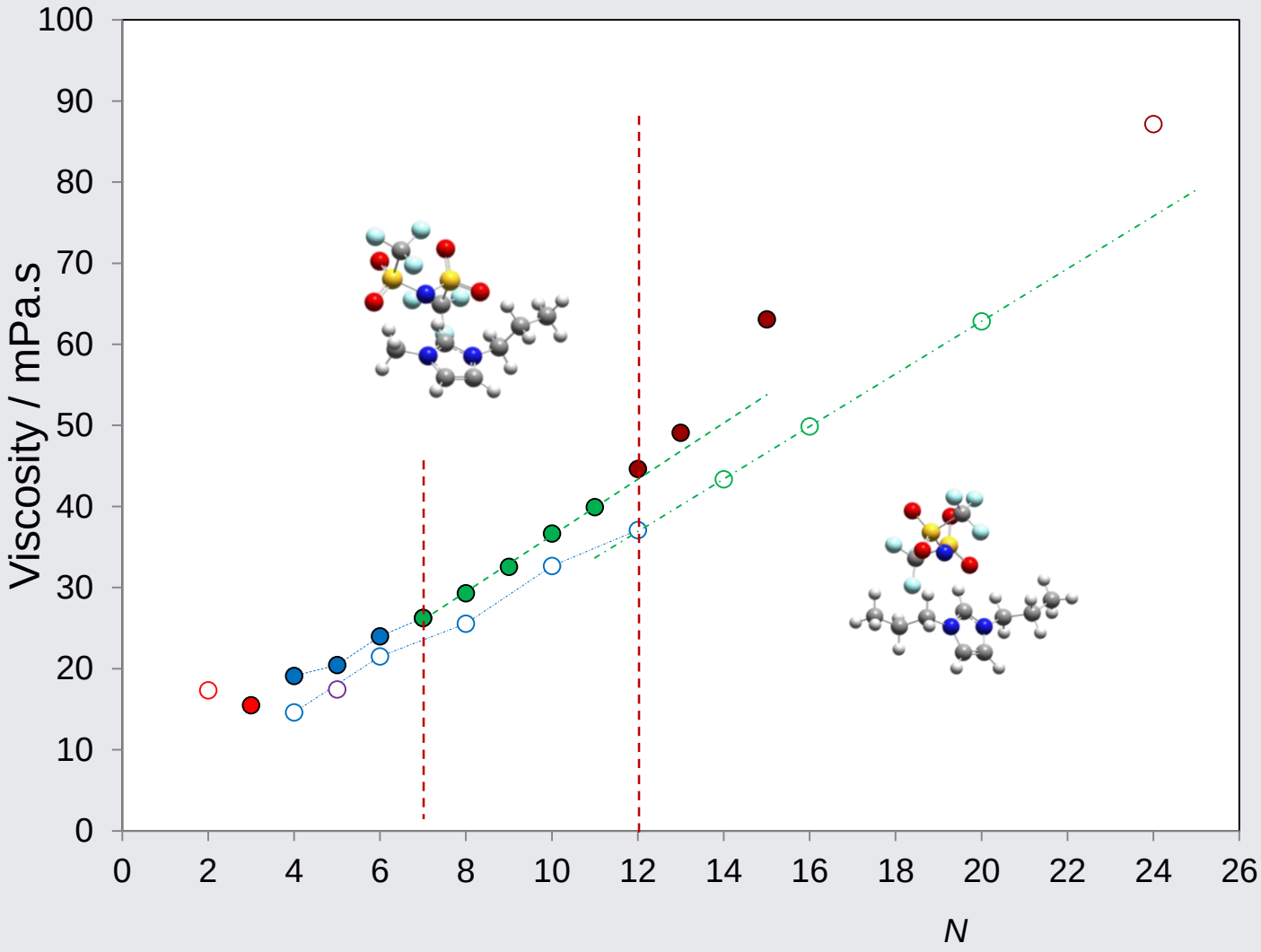


$[C_nC_nim][NTf_2]$ heat capacity



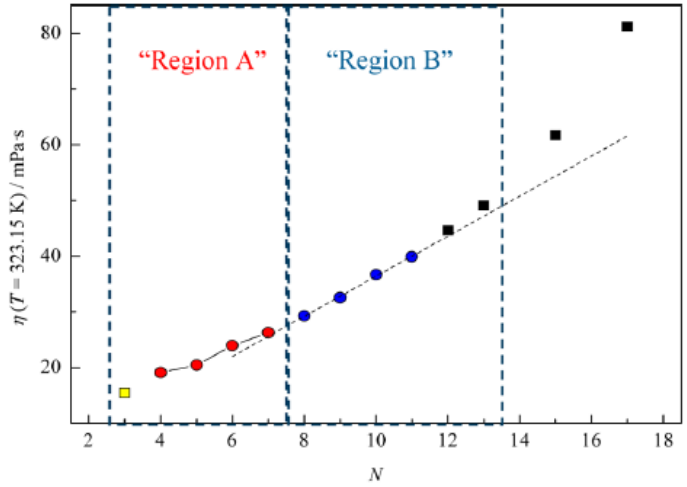


$[C_nC_nim]$ $[NTf_2]$ viscosity



$[C_nC_nim][NTf_2]$ viscosity

The Journal of Physical Chemistry B Article



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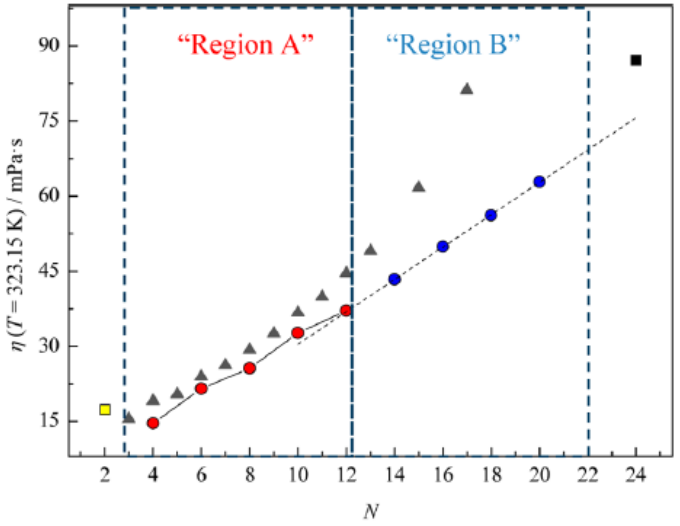
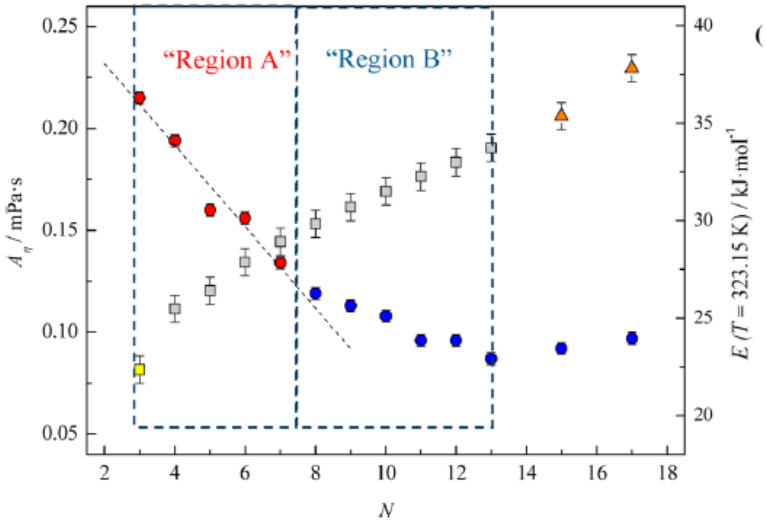
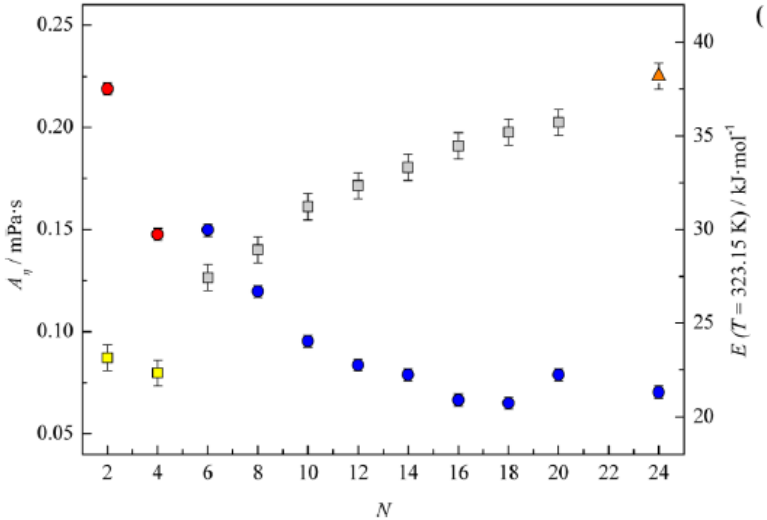


(I)

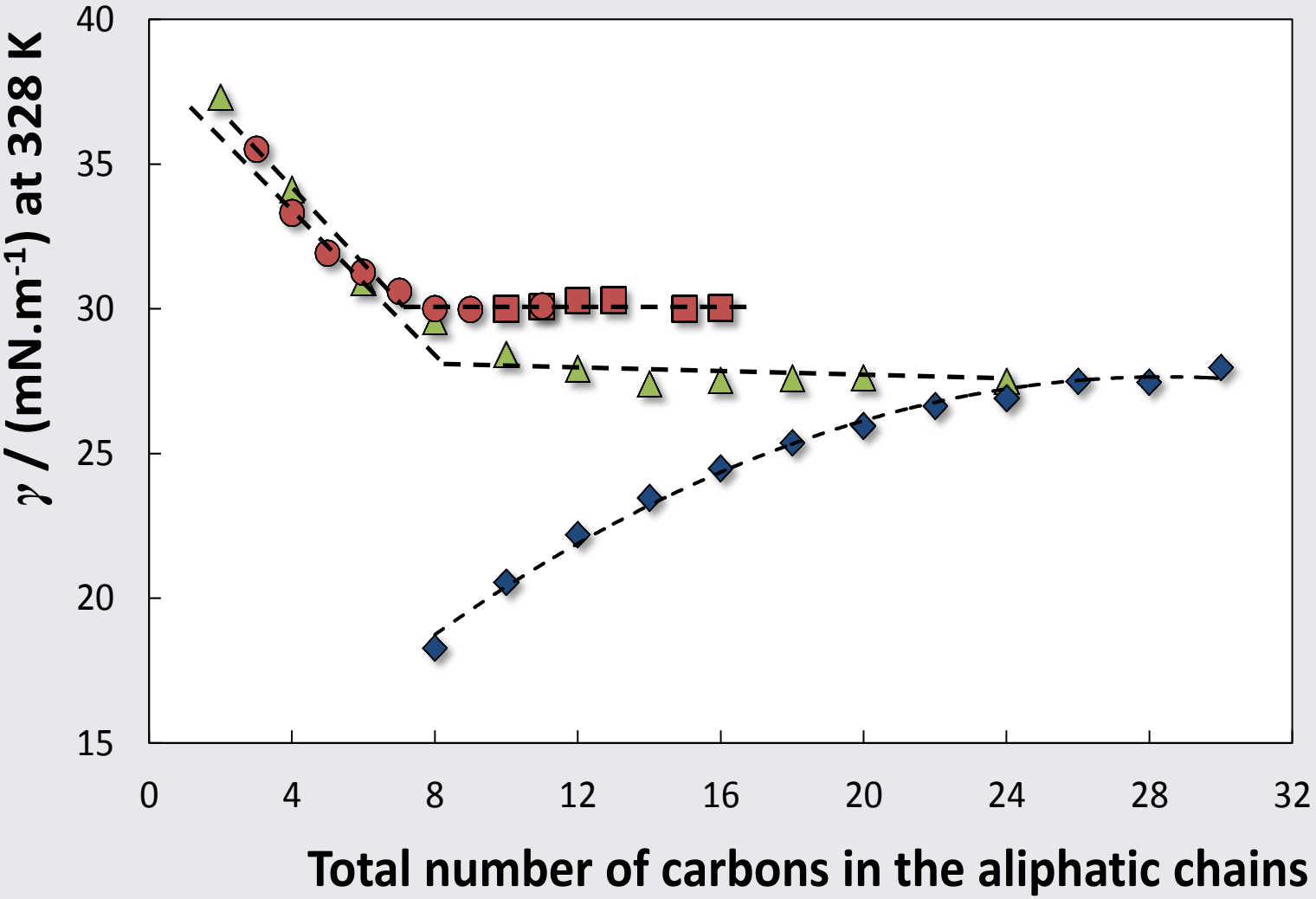


(II)

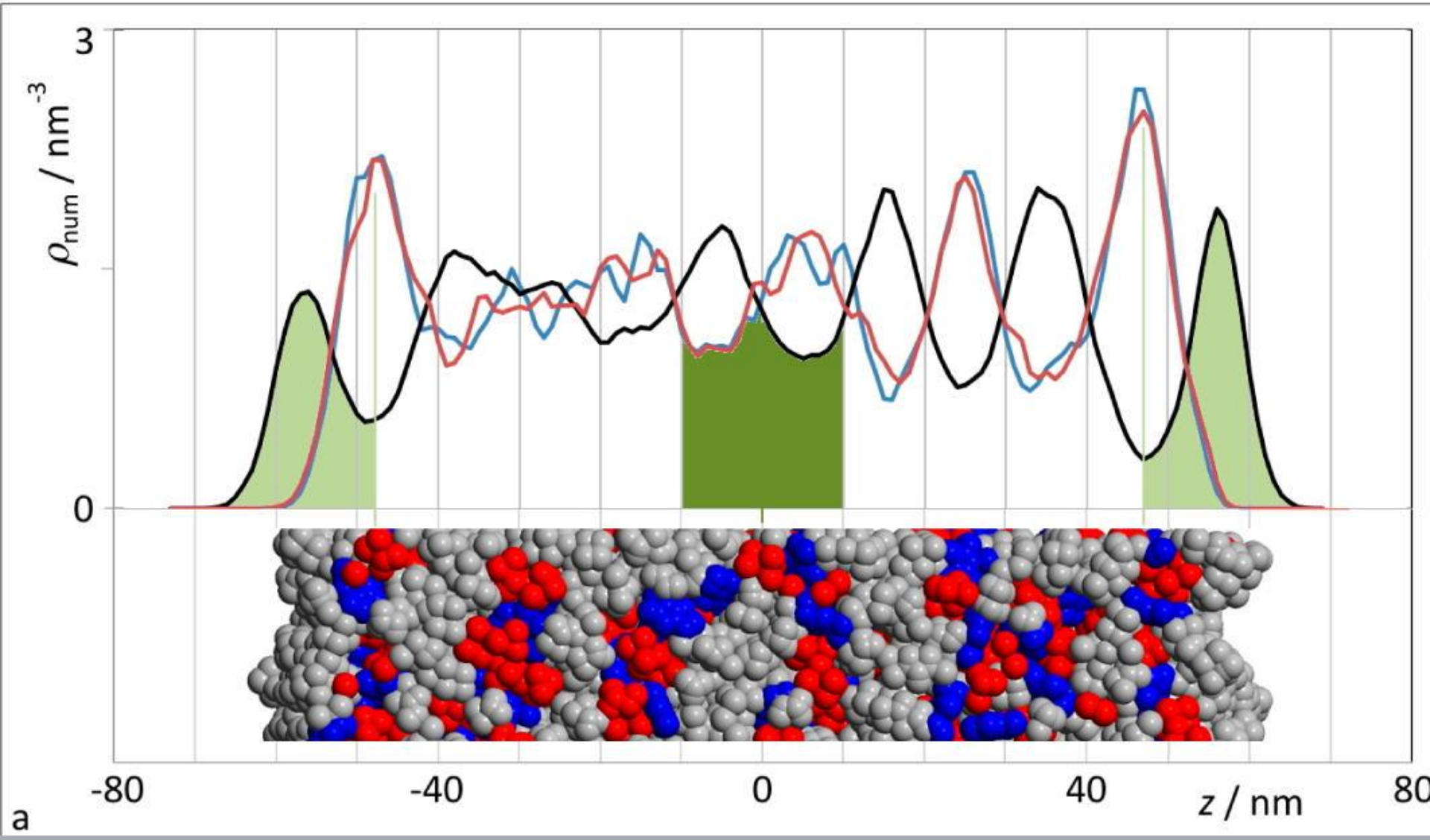


(II)

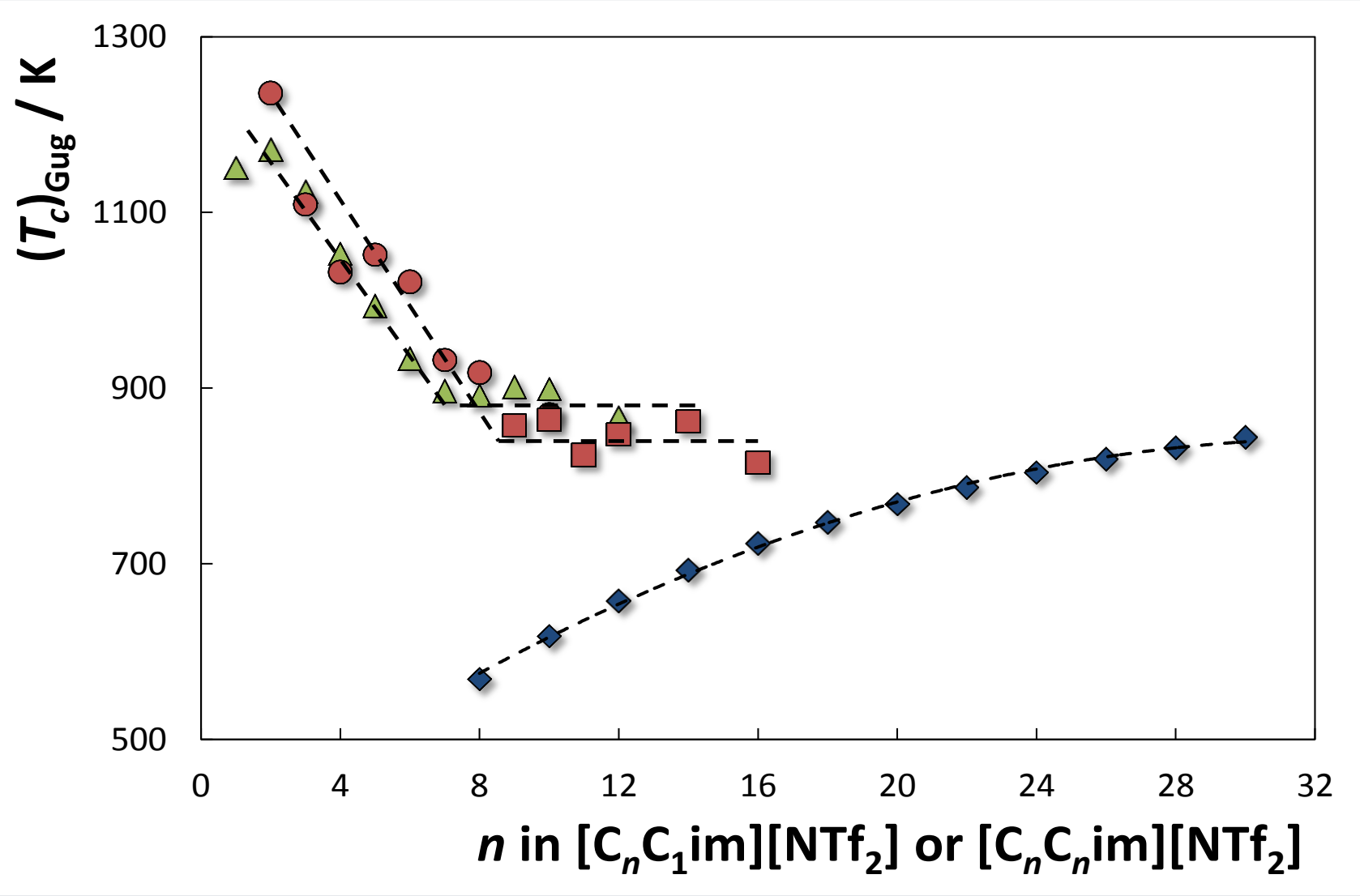
$[C_nC_nim][NTf_2]$ surface tensions



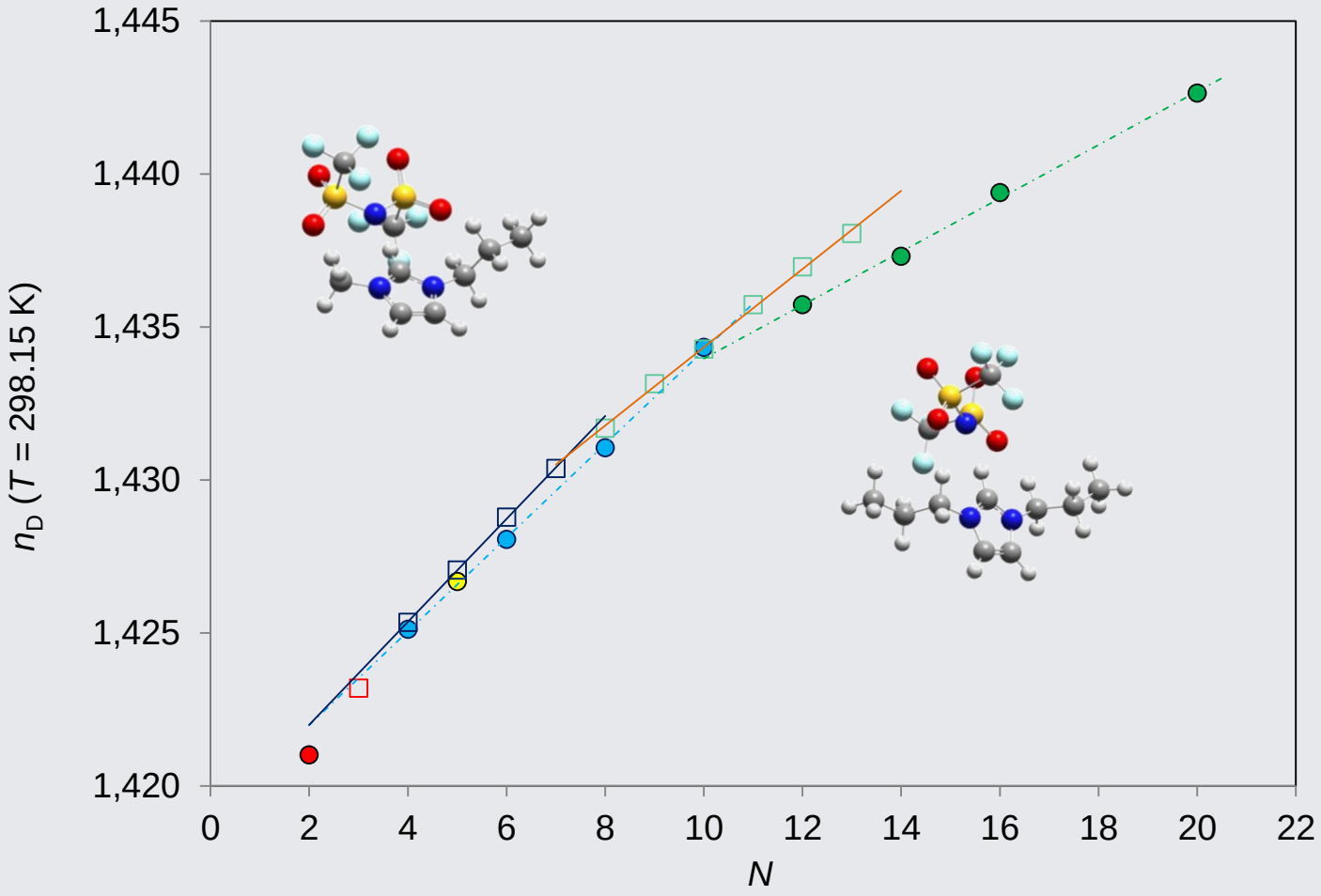
$[C_nC_nim]$ $[NTf_2]$ surface tensions

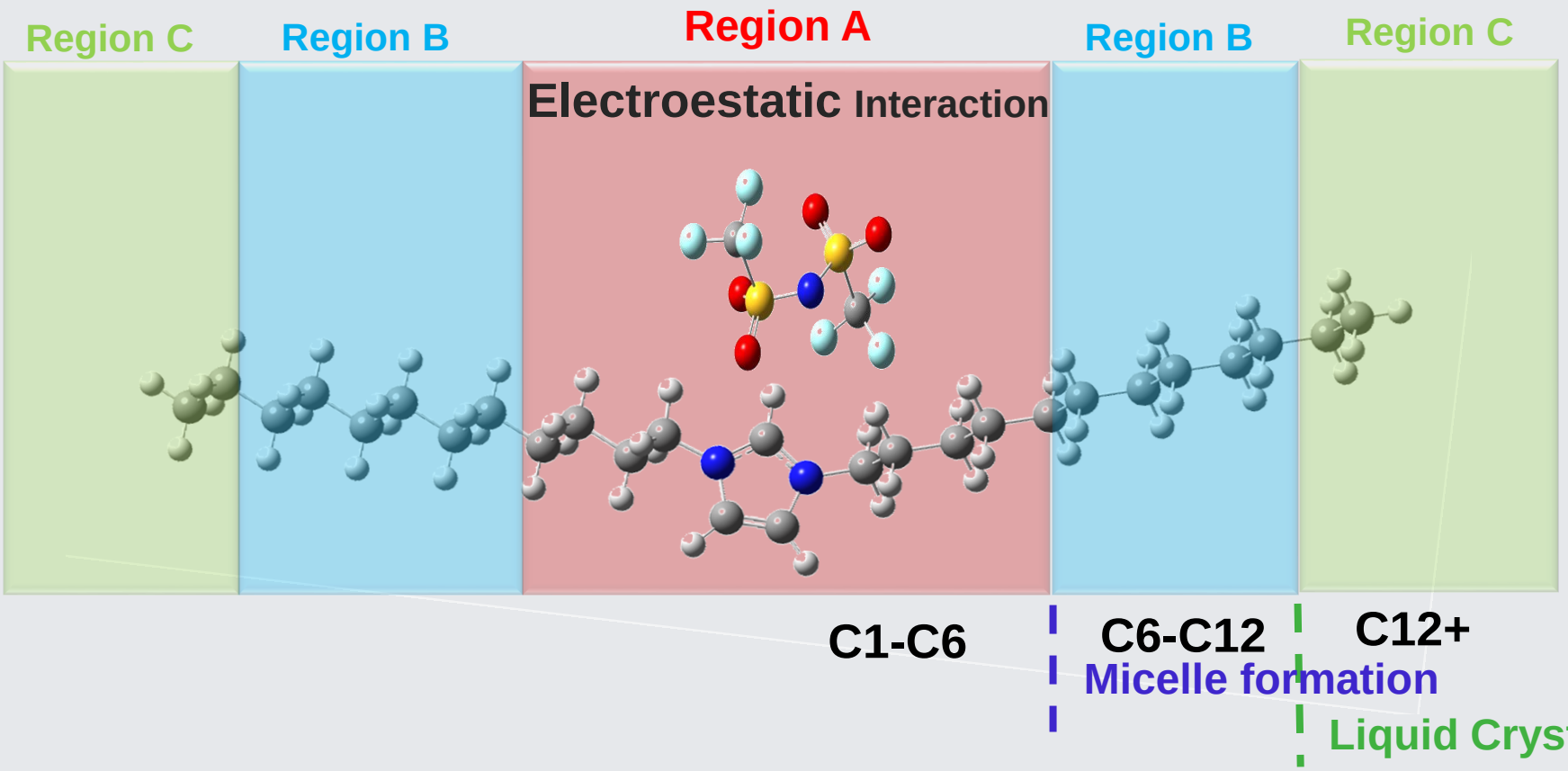


$[C_nC_nim][NTf_2]$ surface tensions



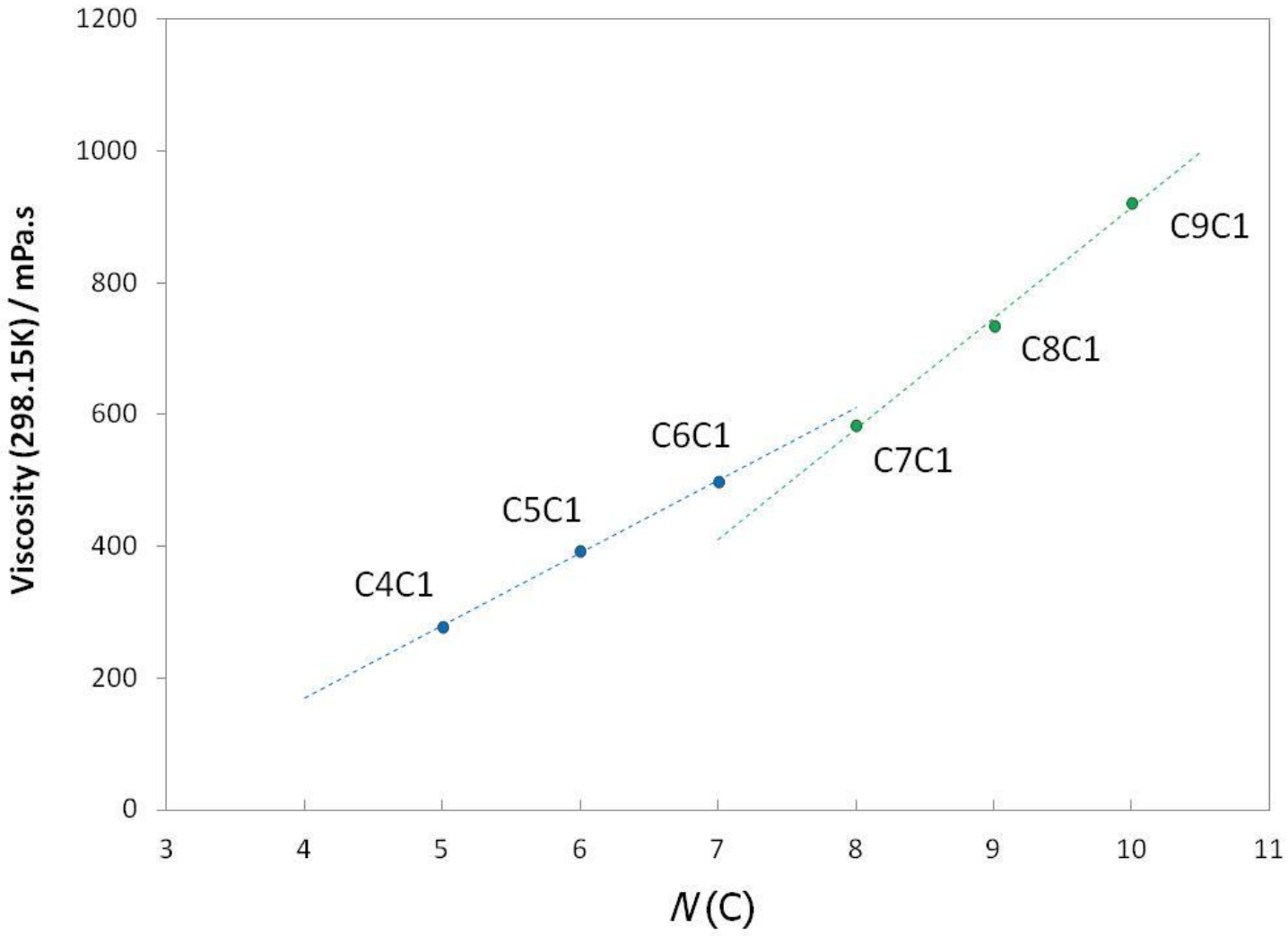
$[C_nC_nim]$ $[NTf_2]$ refractive indexes




Region C
Region B
Region A
Region B
Region C
Electroestatic Interaction
C1-C6
C6-C12
C12+
Micelle formation
Liquid Crystals

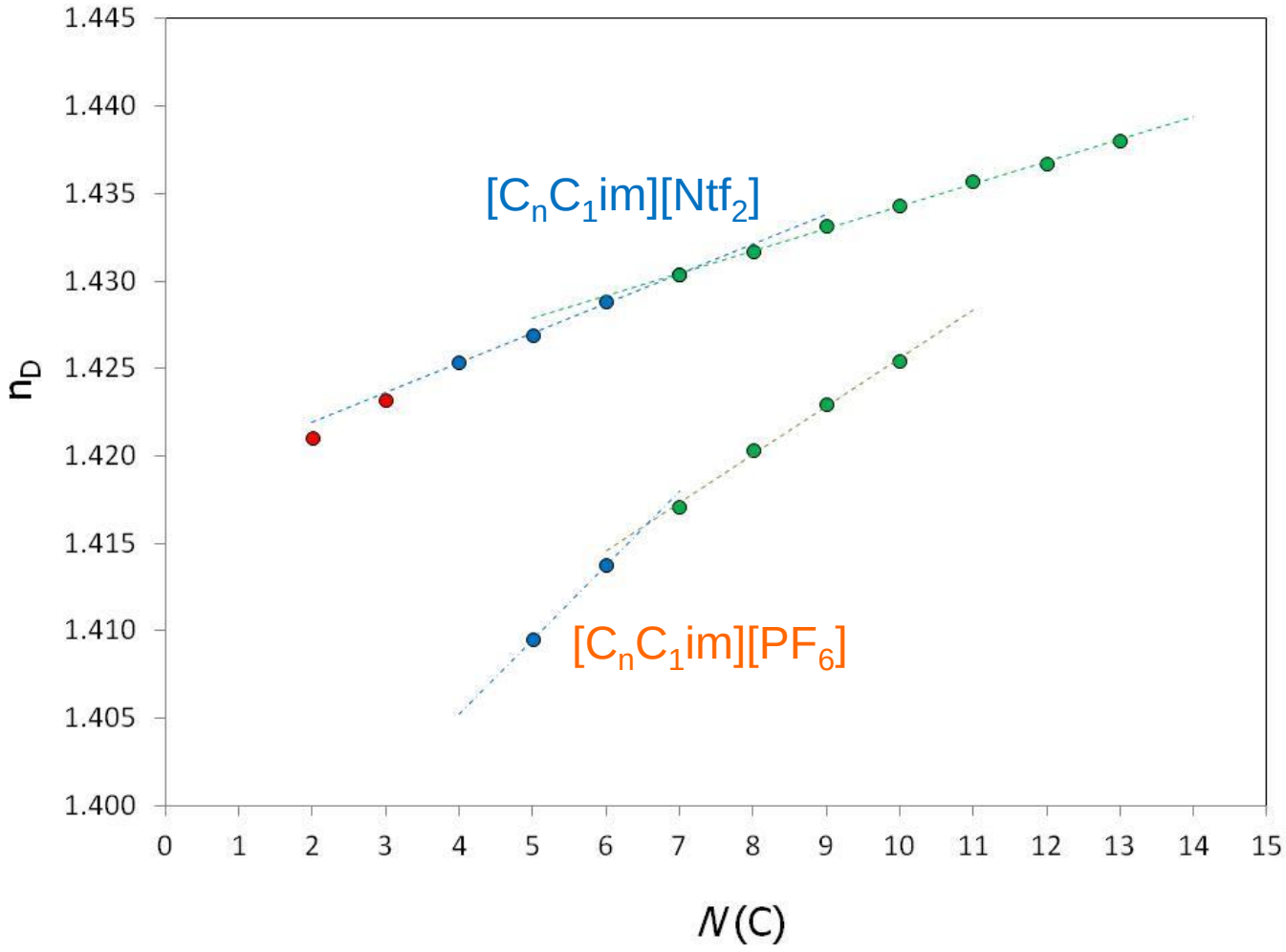
Trend shifts on other ionic liquids

$[C_nC_1im][PF_6]$ viscosities

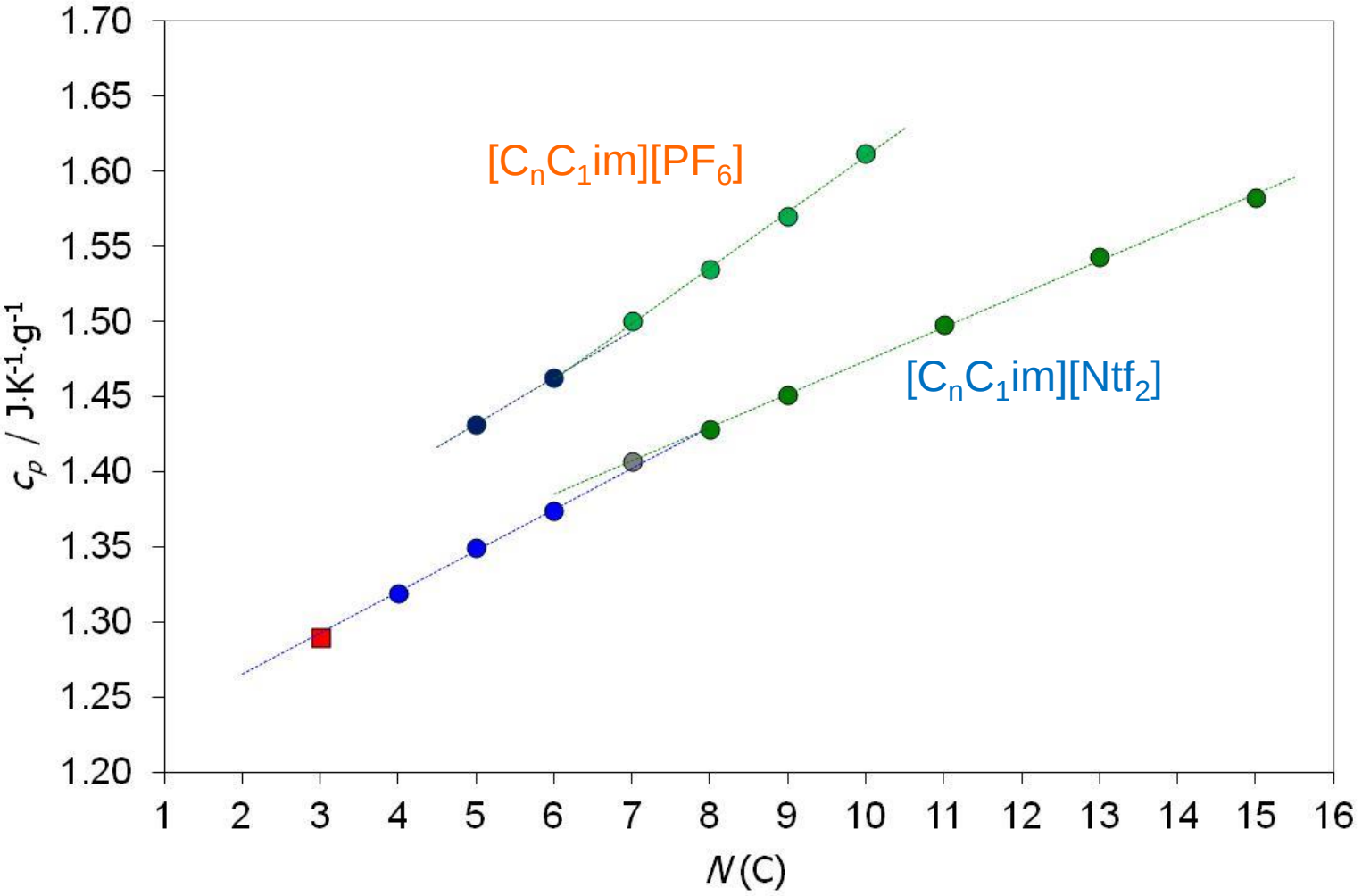


Rocha et al. Journal of Molecular Liquids 188 (2013) 196–202

$[C_nC_1im]$ $[PF_6]$ refraction indexes

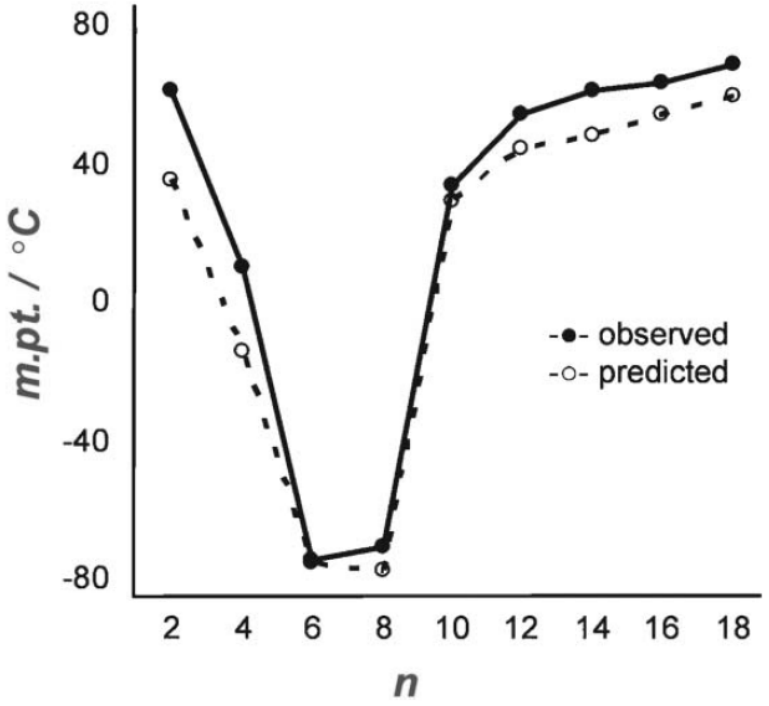


$[C_nC_1im]$ $[PF_6]$ heat capacities



Rocha et al. Unpublished data

$[C_nC_1im]$ $[PF_6]$ melting points



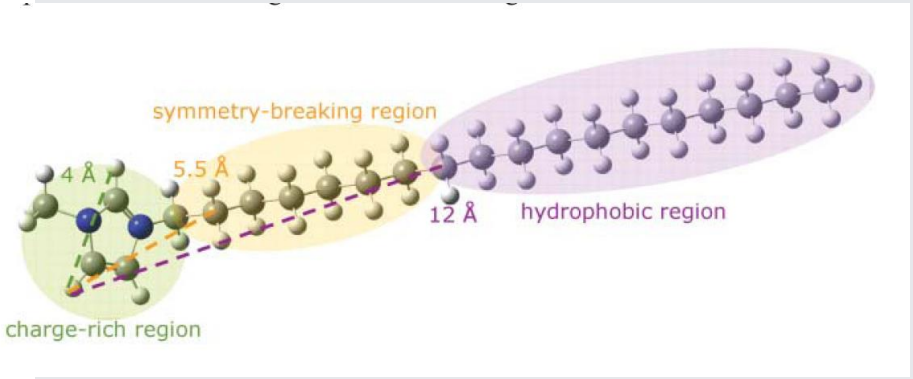


Fig. 11 Predicted and observed melting points for a series of 1-alkyl-3-methylimidazolium hexafluorophosphate, $[C_n\text{mim}][PF_6]$, ionic liquids with increasing carbon chain length on the cation.[43]

CRITICAL REVIEW www.rsc.org/csr | Chemical Society Reviews

Applications of ionic liquids in the chemical industry

Natalia V. Plechkova[a] and Kenneth R. Seddon[ab]

[P_{888n}] Cl densities

Dalton
Transact

Cite this: *Dalton*

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**Alkyltriocty
physicochem**

Gabriela Adamov

Received 25th Februa
DOI: 10.1039/c1dt10

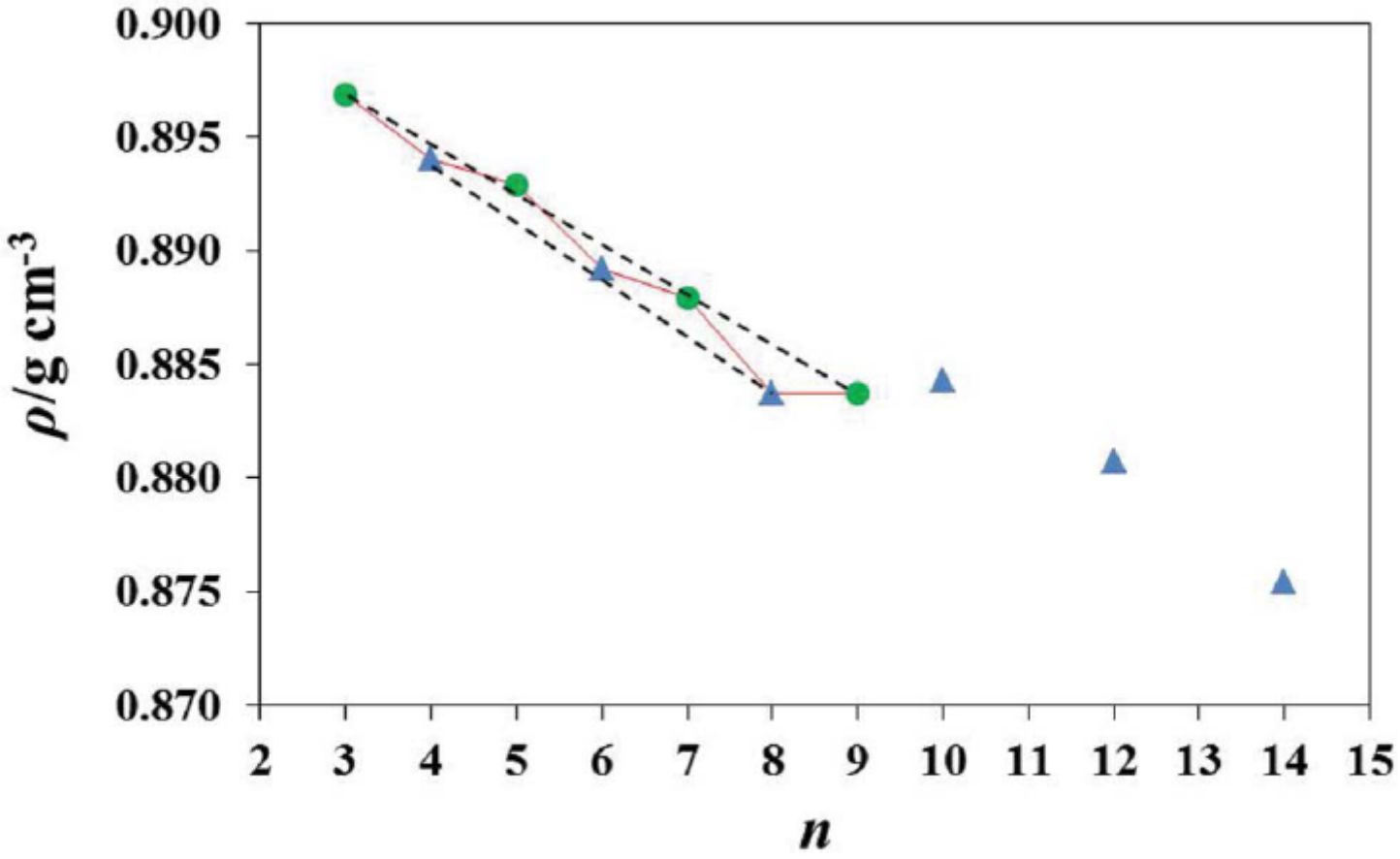
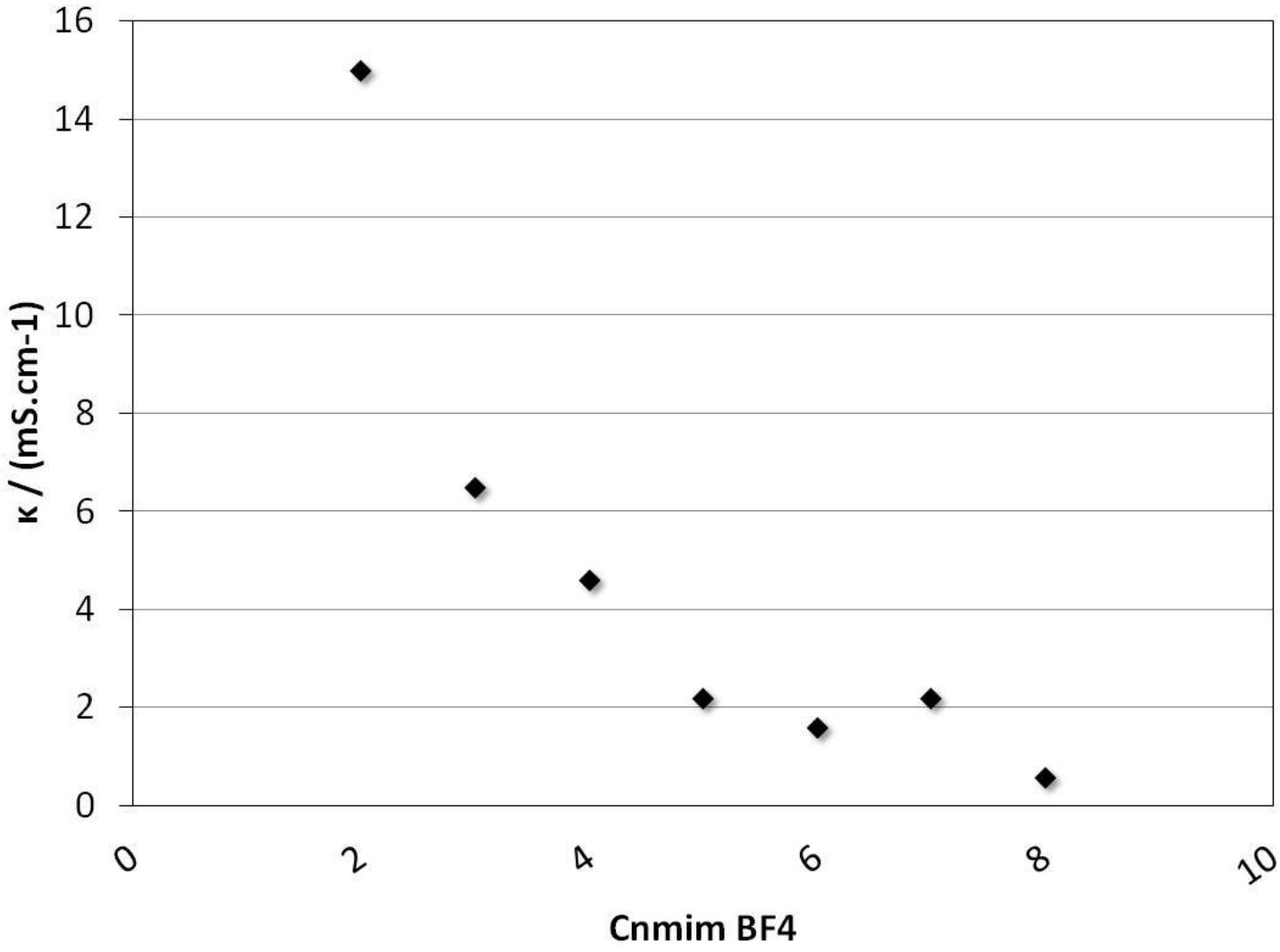


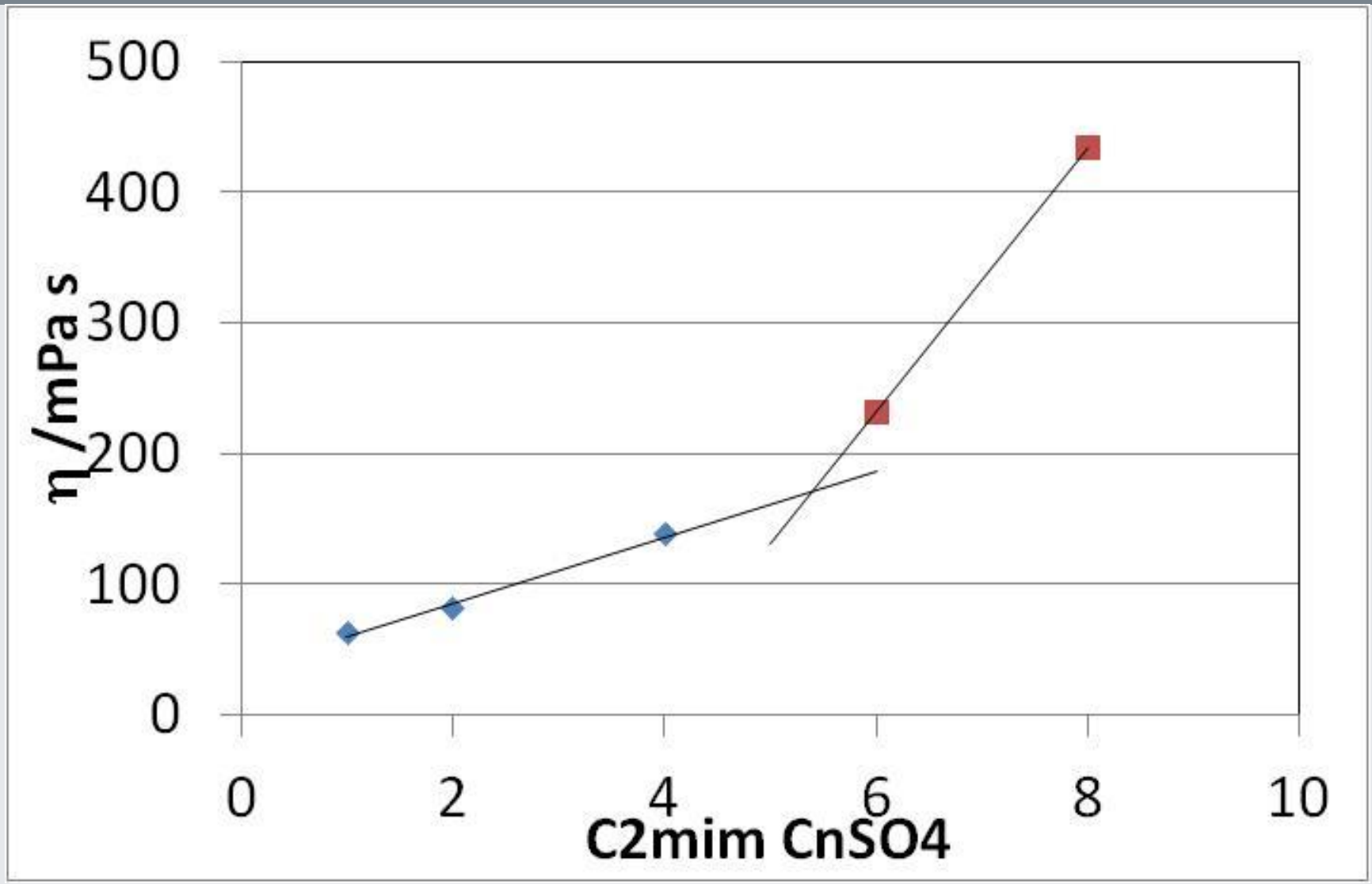
Fig. 11 Experimental densities of [P_{888n}]Cl ionic liquids at 30 °C, where $n = 3$, 5, 7 and 9 (●), $n = 4$, 6, 8, 10, 12 and 14 (▲).

$[C_nmim]\ [BF_4]$ conductivities



Trend shifts on anions

$[C_2C_1im]$ $[C_nSO_4]$ viscosity



Costa et al. J. Chem. Eng. Data, 56, 3433–3441, 2011

Trend shifts on phase equilibria

Water solubility in $[C_nC_1im]$ $[NTf_2]$

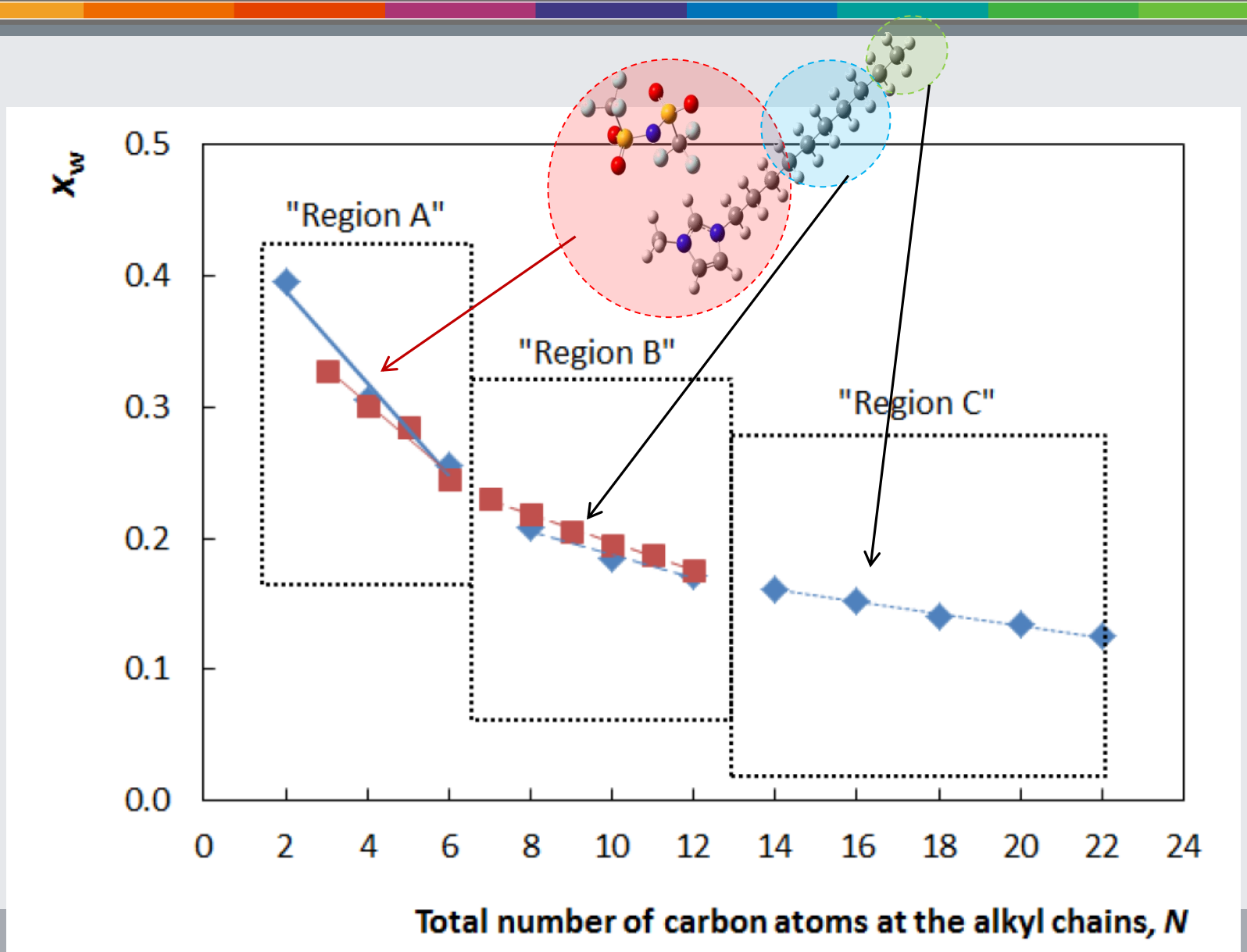
Mutual Solubilities of Water and the $[C_n mim][Tf_2N]$ Hydrophobic Ionic Liquids

Mara G. Freire,[†] Pedro J. Carvalho,[†] Ramesh L. Gardas,[†] Isabel M. Marrucho,[†] Luís M. N. B. F. Santos,[‡] and João A. P. Coutinho*,[†]

CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal, and CIQ, Departamento de Química, Faculdade de Ciências da Universidade do Porto, R. Campo Alegre 687, 4169-007 Porto, Portugal

Received: October 4, 2007; In Final Form: November 13, 2007

Water solubility in $[C_nC_1im][NTf_2]$



Light alkanes solubility in $[C_nC_1im]$ $[NTf_2]$

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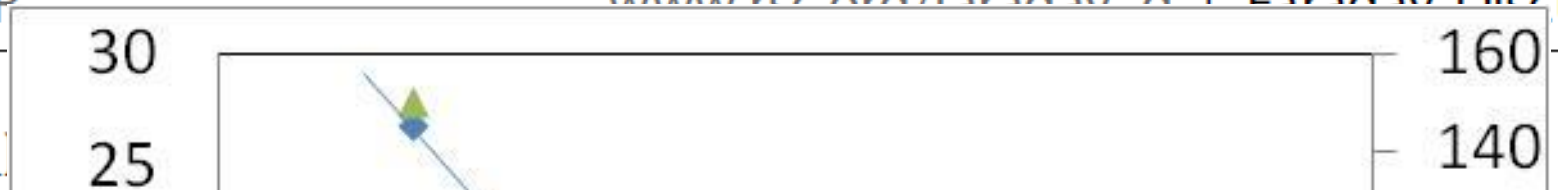

Table 4 Thermodynamic properties of solvation of ethane and *n*-butane in $[C_nC_1Im][NTf_2]$ ionic liquids in the temperature range studied

Ionic liquid	$\Delta_{solv}H^{\infty}$ kJ mol^{-1}	$\Delta_{solv}S^{\infty}$ J mol^{-1} K^{-1}	Ionic liquid	$\Delta_{solv}H^{\infty}$ kJ mol^{-1}	$\Delta_{solv}S^{\infty}$ J mol^{-1} K^{-1}
	C_2H_6			C_4H_{10}	
$[C_2C_1Im][NTf_2]$	-12 ± 1	-80 ± 3	$[C_2C_1Im][NTf_2]$	-20 ± 2	-92 ± 4
$[C_4C_1Im][NTf_2]$	-13 ± 1	-81 ± 3	$[C_4C_1Im][NTf_2]$	-20 ± 2	-90 ± 4
$[C_6C_1Im][NTf_2]$	-10 ± 1	-69 ± 2	$[C_6C_1Im][NTf_2]$	-20 ± 2	-83 ± 3
$[C_8C_1Im][NTf_2]$	-13 ± 1	-76 ± 3	$[C_8C_1Im][NTf_2]$	-21 ± 2	-86 ± 4
$[C_{10}C_1Im][NTf_2]$	-12 ± 1	-74 ± 2	$[C_{10}C_1Im][NTf_2]$	-21 ± 2	-85 ± 4

$$\Delta_{solv}S^{\infty} = (\Delta_{solv}H^{\infty} - \Delta_{solv}G^{\infty})/T = -RT\partial/\partial T\left[\ln\left(K_H/p^0\right)\right] - R\ln\left(K_H/p^0\right) \quad (6)$$

$[C_nC_1im]$ $[NTf_2]$-alkanols phase diagrams

DOI: 10.1002

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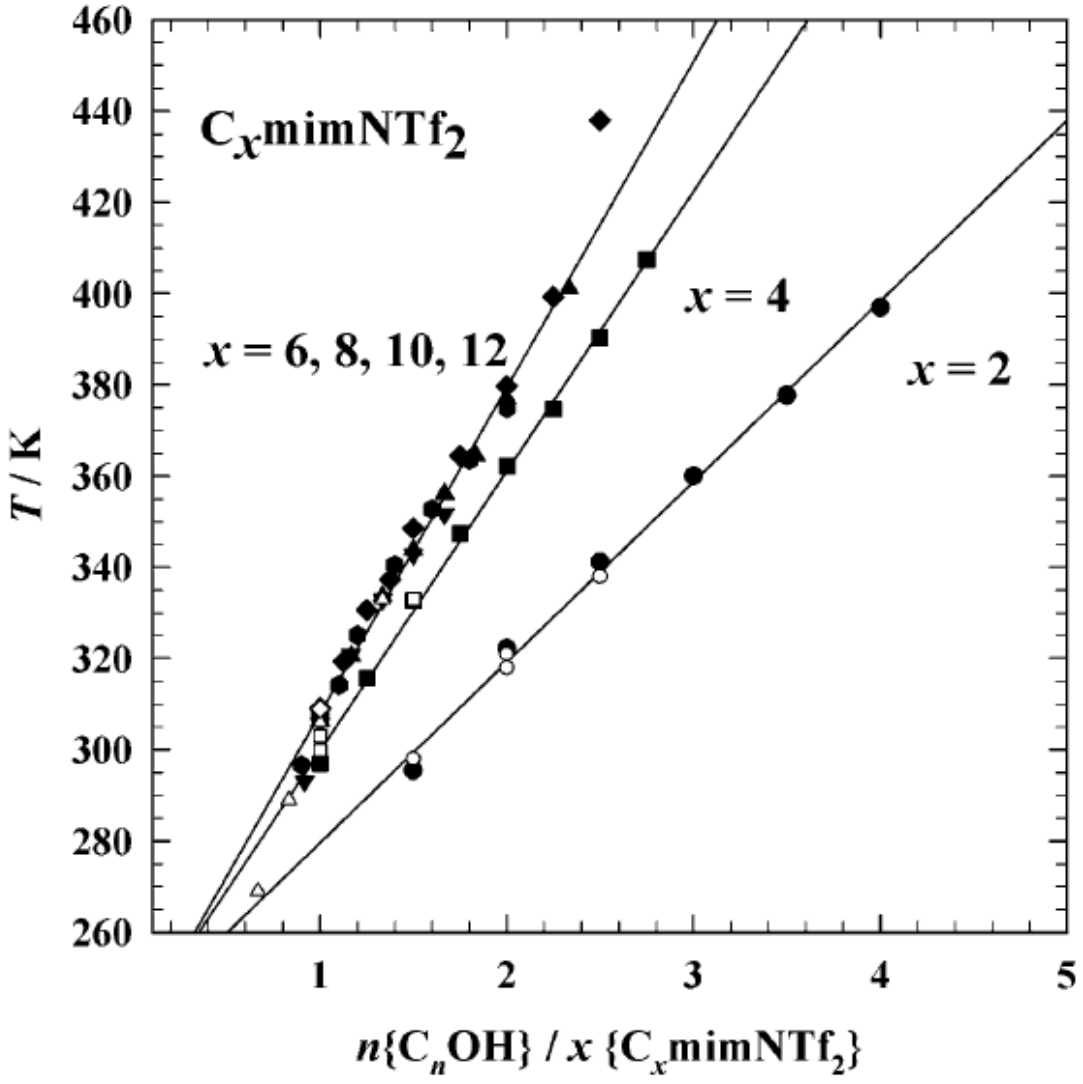
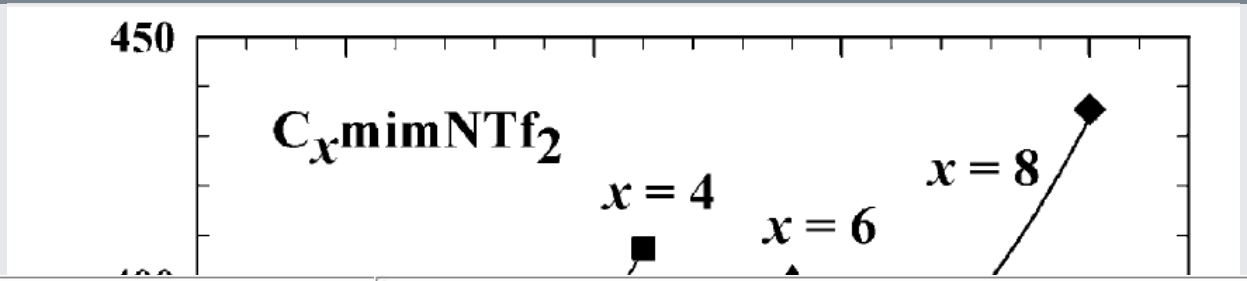
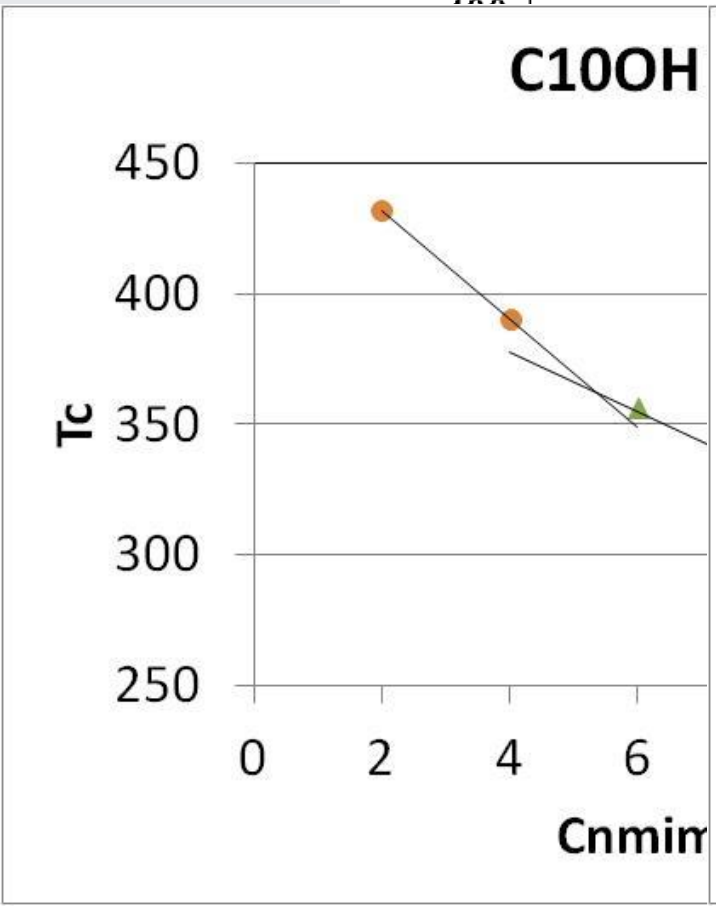


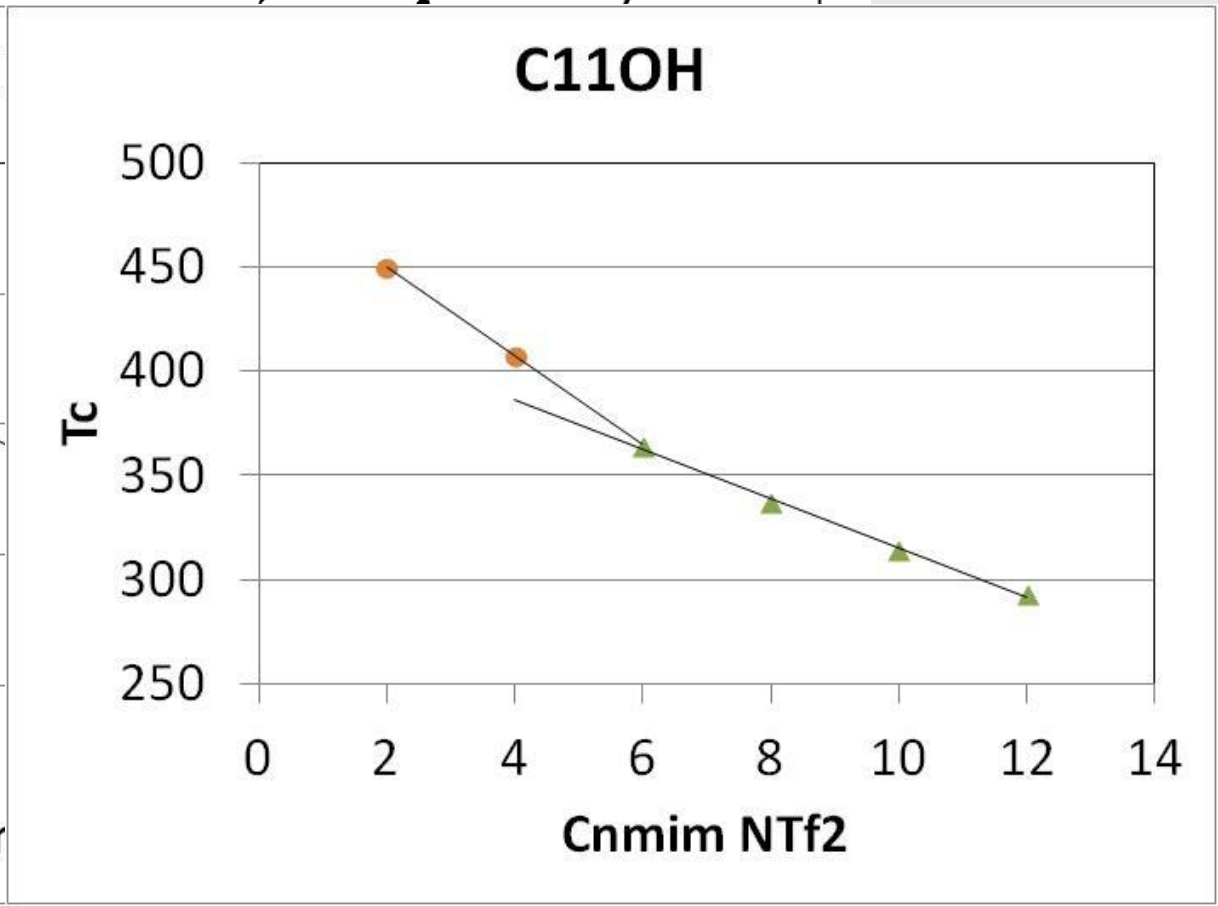
The liquid–lic … plete scaling of 1-ethyl-3- … osition, width amide (C_2mim … ed with simi- described. By … onding state determined c … st 45 individ- pressure. Par … navior of this atures (UCST) … A simple em- chain length … description of lyzed numeri … king the ratio the descriptic … lkyl-3-methyl- suming the v … t.

Figure 7. Dependence of the UCST for all of the systems shown in Figure 6

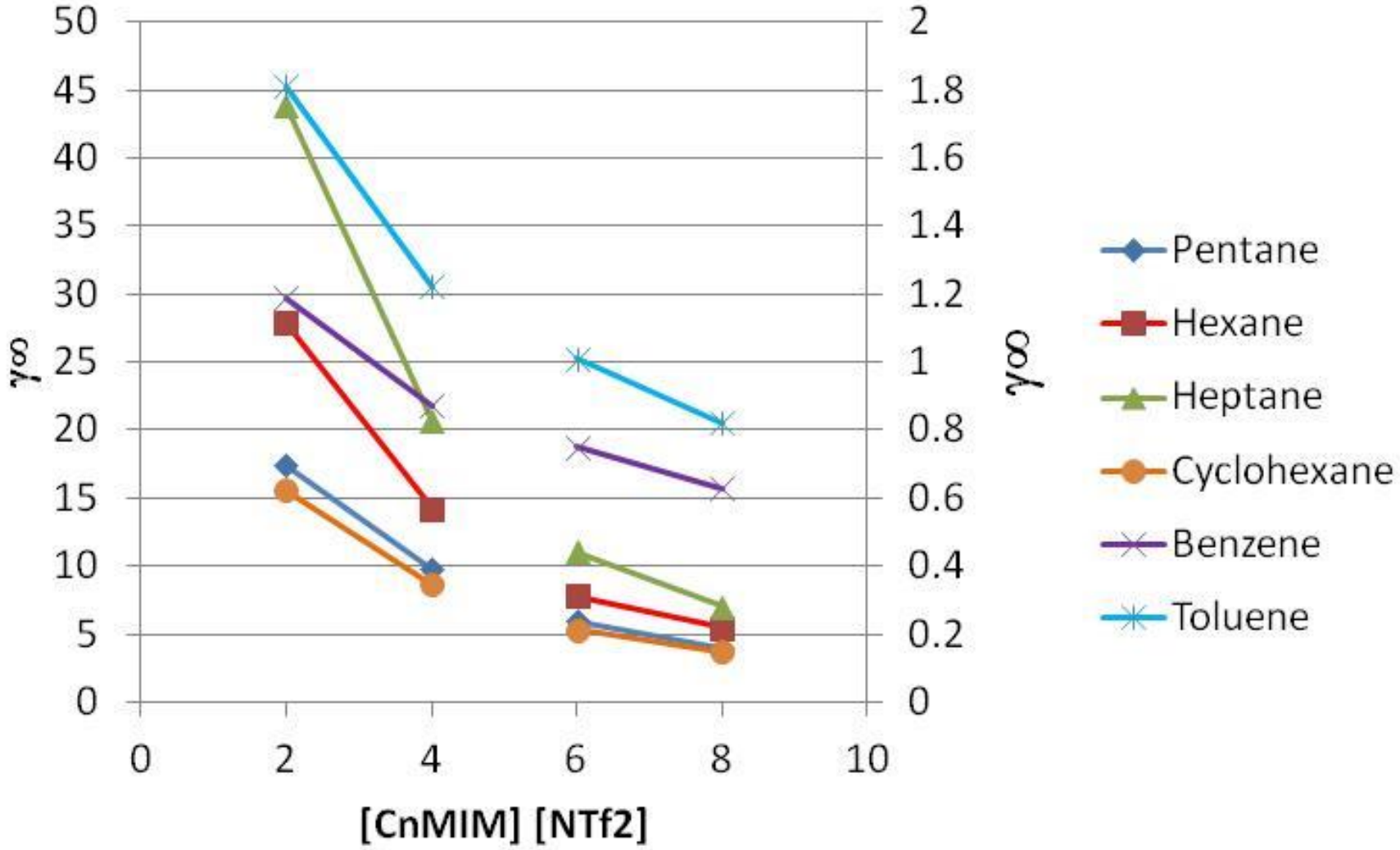
$[C_nC_1im]$ $[NTf_2]$-alkanols phase diagrams





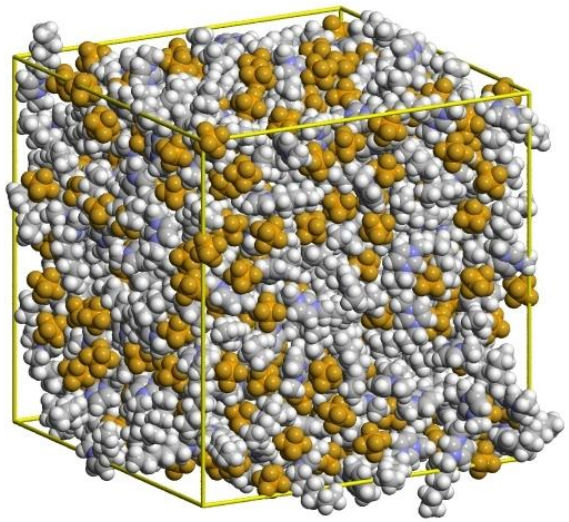


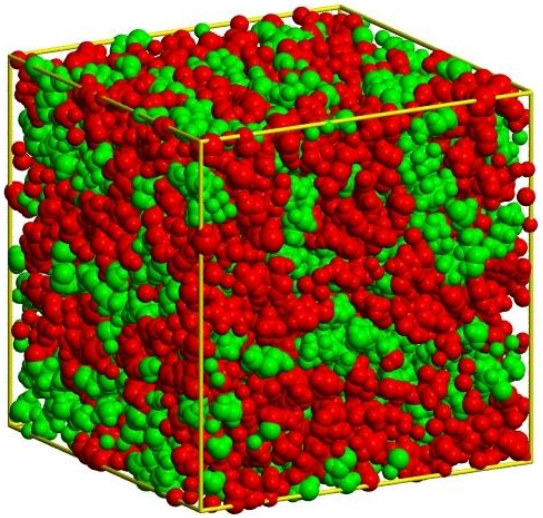
Infinite dilution activity coefficients

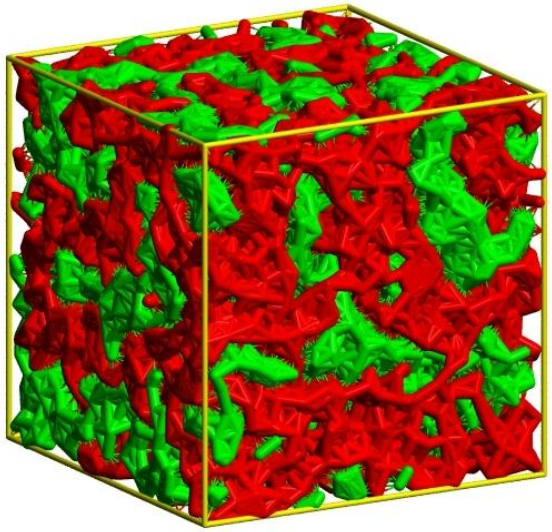


Gmehling et al., 2005

Nanostructural organization in ionic liquids







A.H. Pádua e J.N.Canongia Lopes, 2006

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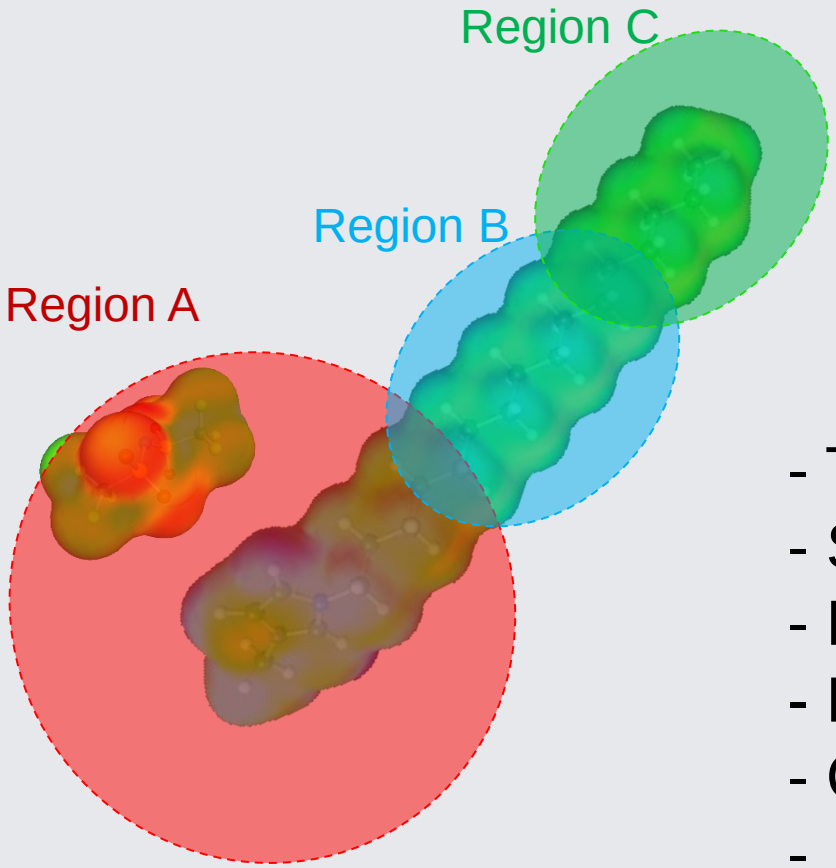
Trend shifts on other properties

Nanostructure and Ionic liquids properties



- Thermophysical properties
- Solvation
- Phase diagrams
- Reactivity
- Catalic properties
- ...

Ionic liquids cation-anion interaction

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Evaluation of Cation–Anion Interaction Strength in Ionic Liquids

Ana M. Fernandes,*
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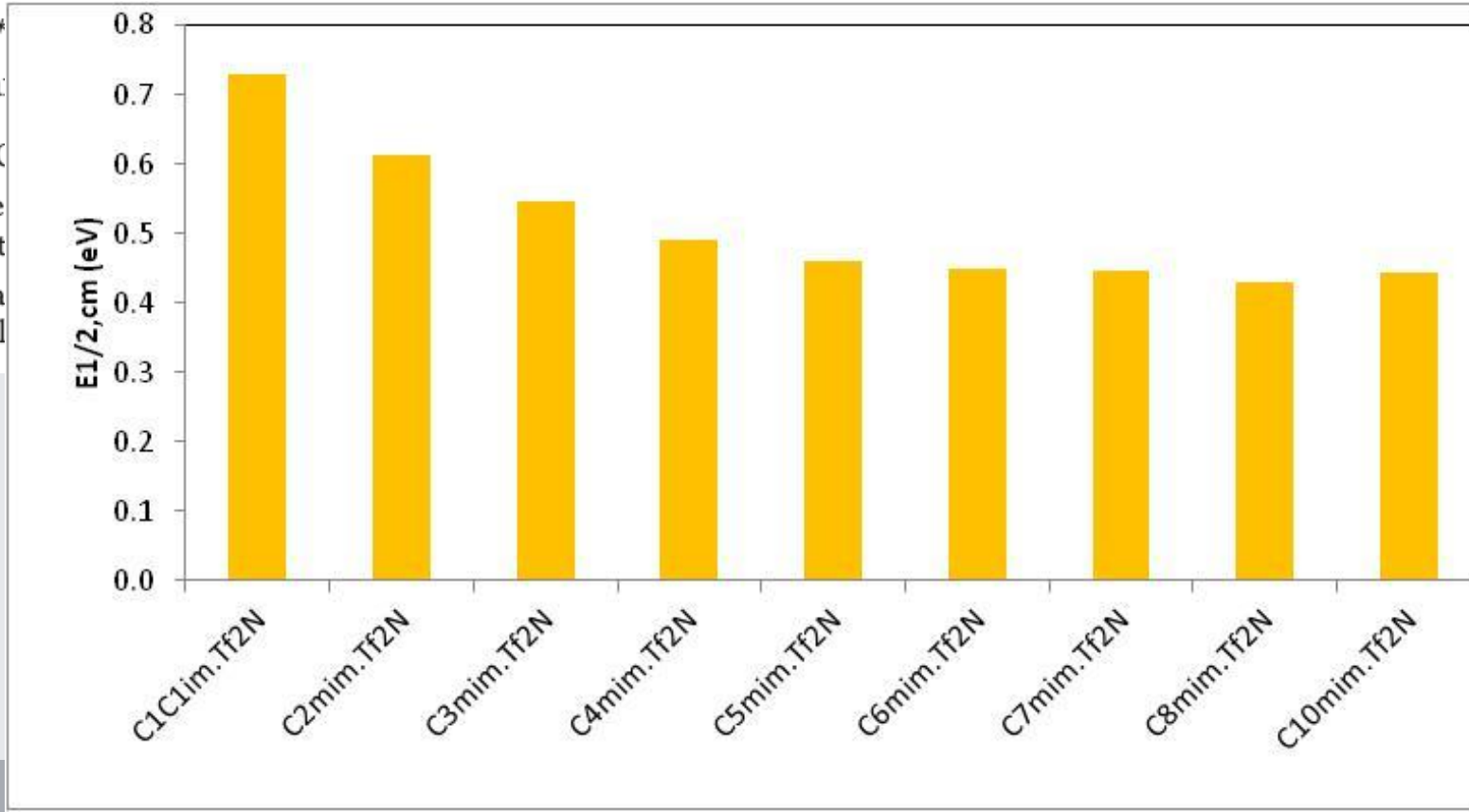
‡CIQ, Departamento de
P-4169-007 Porto, Port
∥Instituto de Tecnologia
Portugal, www.itqb.unl



Ionic liquids cation-anion interaction

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Evaluation of Cation–Anion Interaction Strength in Ionic Liquids

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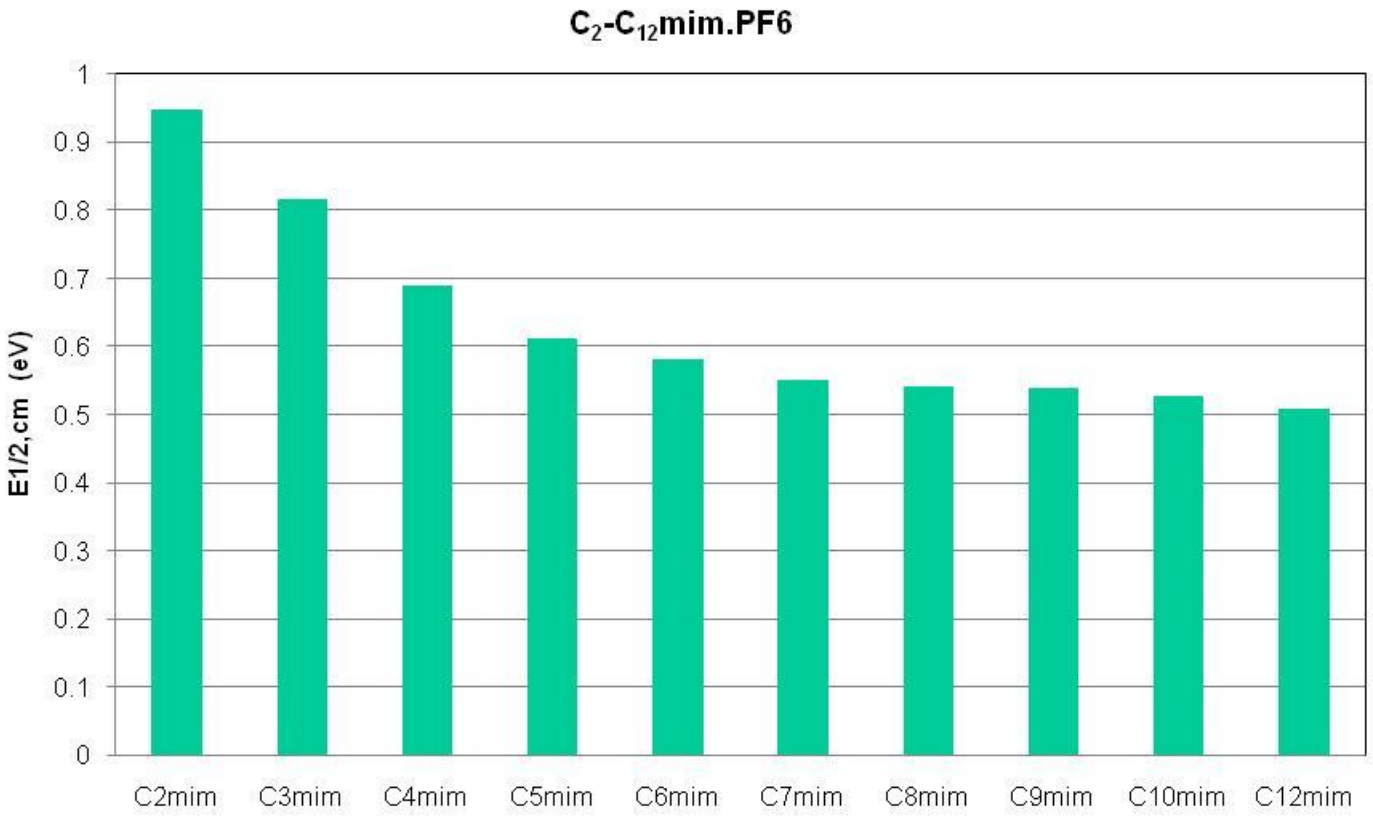
Luís M. N. B. F. Santos‡

†QOPNA and §CICECO, Depart
‡CIQ, Departamento de Química
P-4169-007 Porto, Portugal
∥Instituto de Tecnologia Química
Portugal, www.itqb.unl.pt



Formation of IL-ABS

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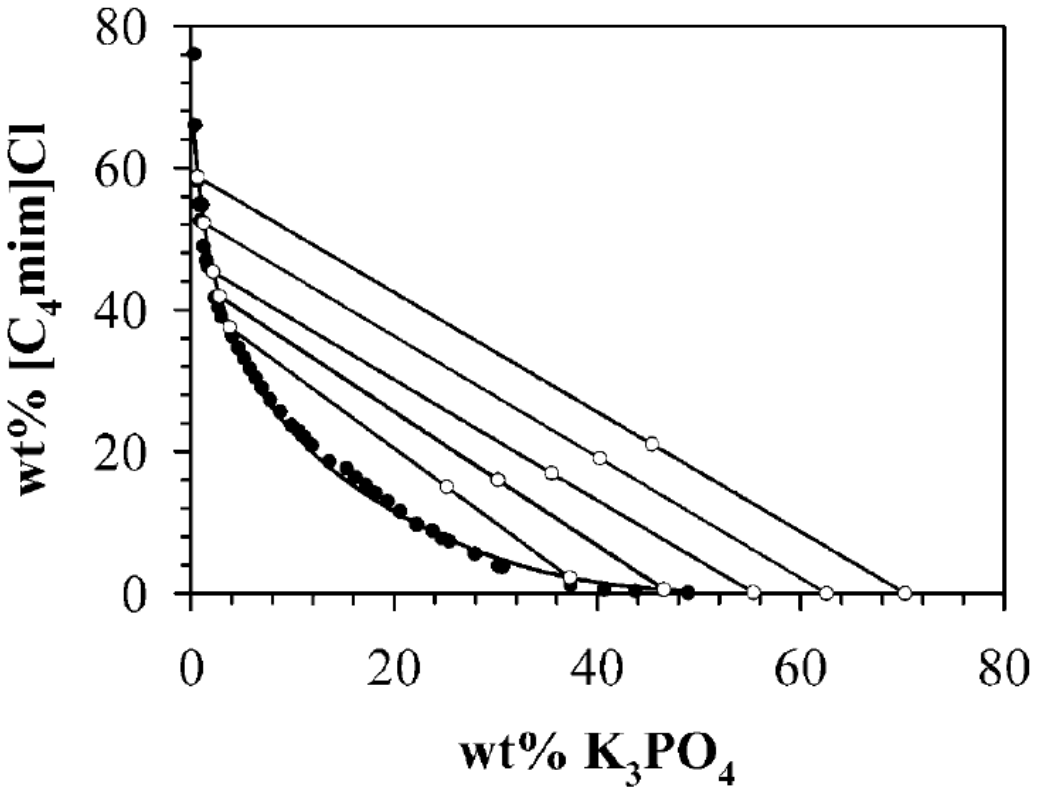

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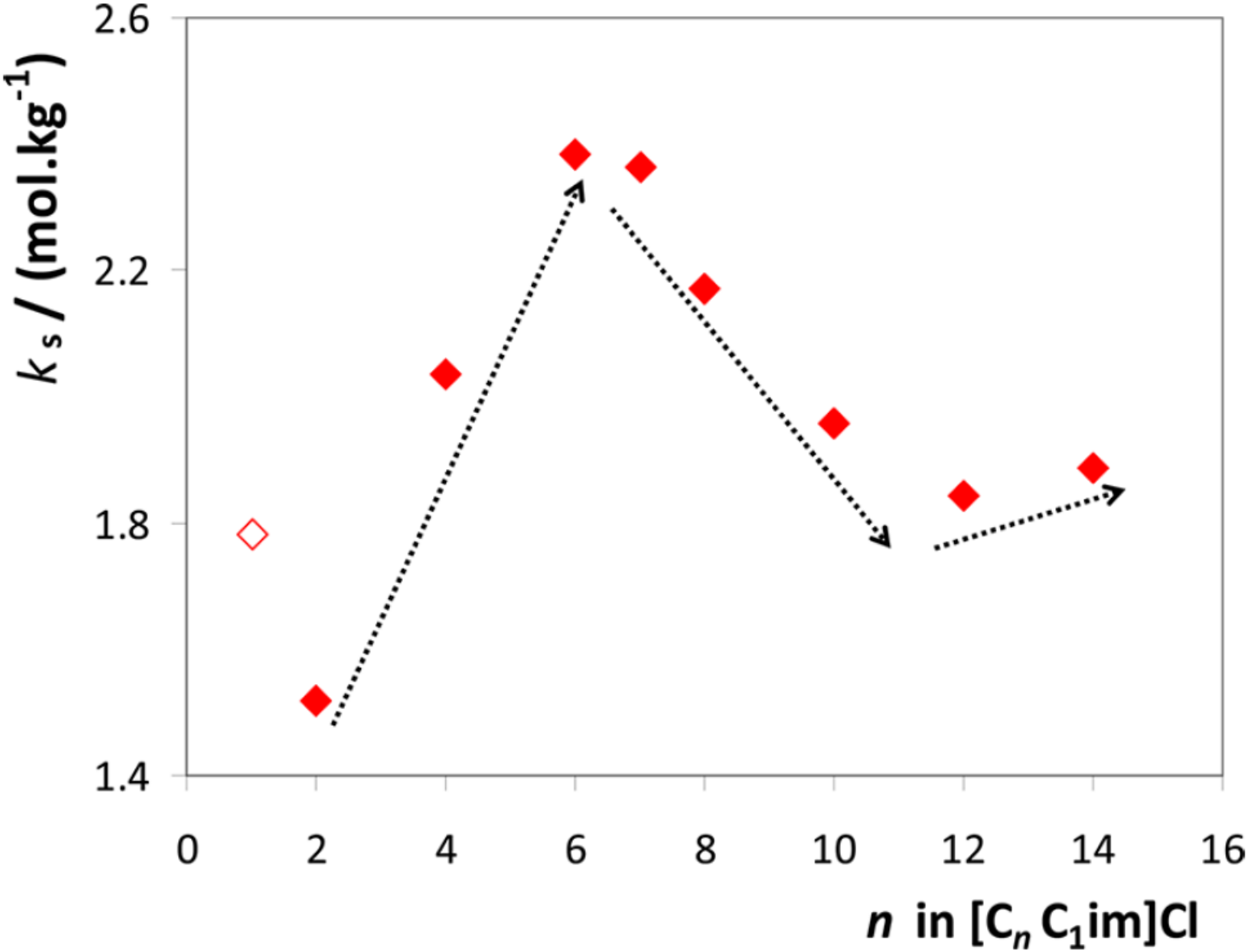
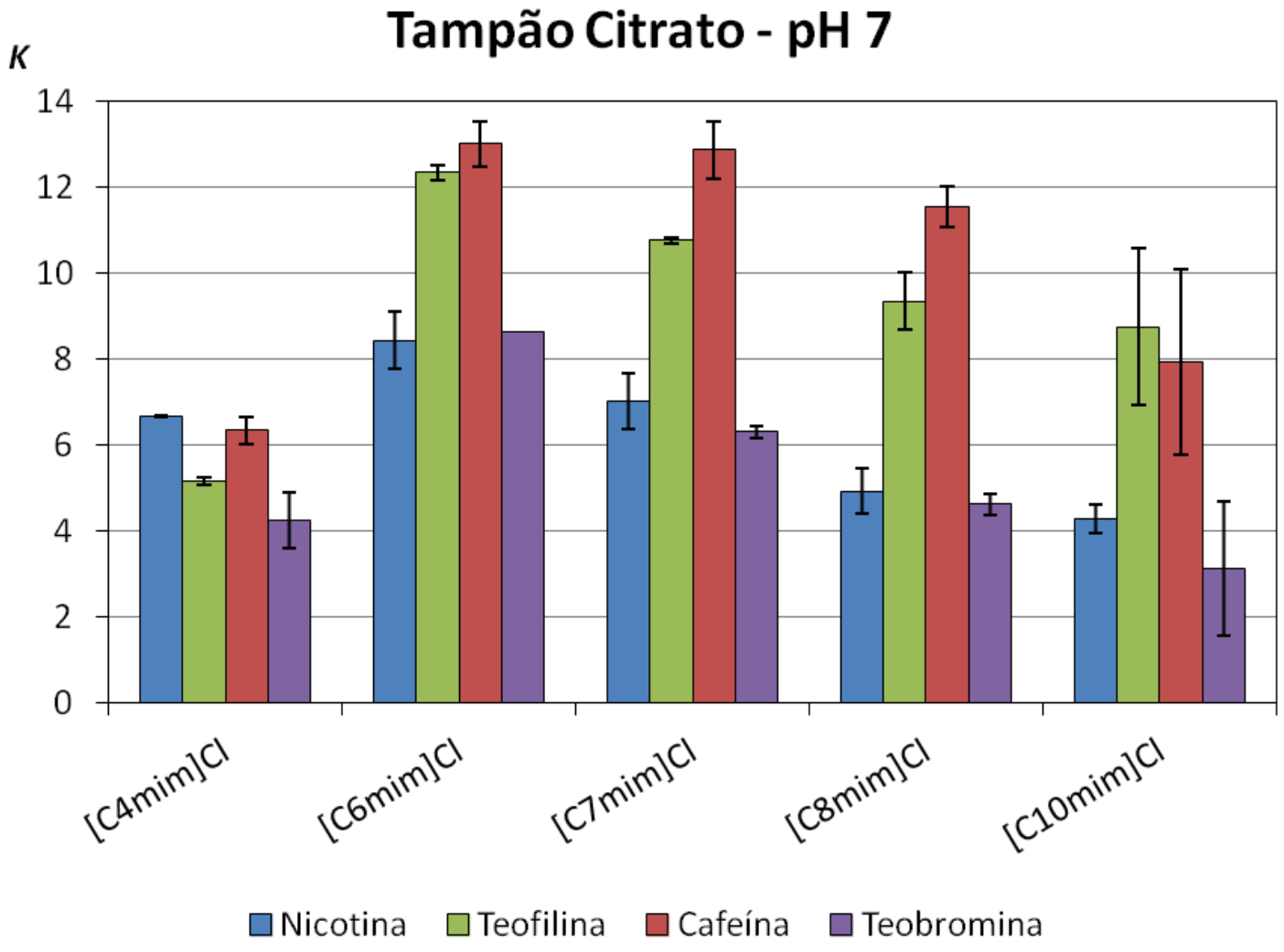
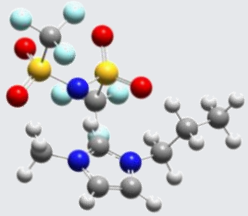
Formation of IL-ABS



Extraction in IL-ABS



Solvation of alcohols in ILs

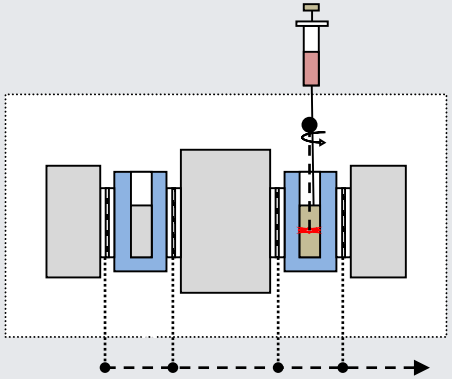


$[C_{N-1}C_1im][NTf_2]$

Alkyl side chain length
(*N* = 3 – 13)

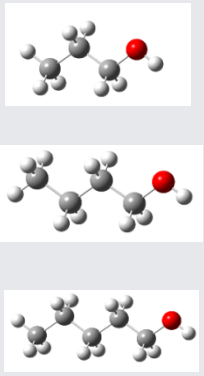
Isothermal Titration Calorimetry , ITC

Solvation of alcohols in Ionic Liquids



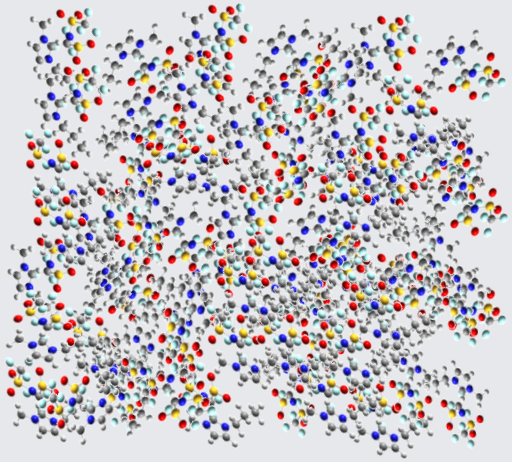
Heat Flux Signal

Alcohols

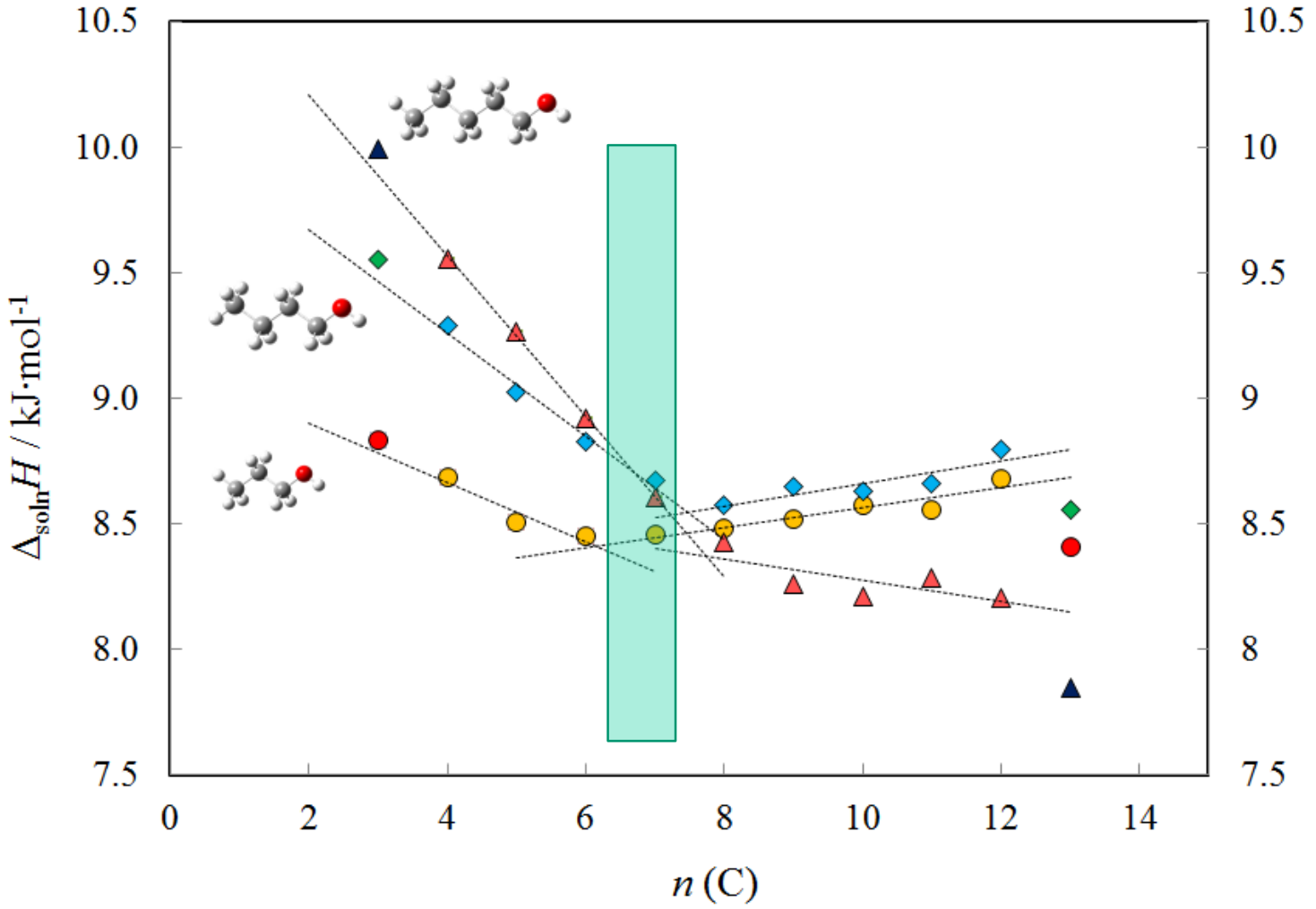


Solvation

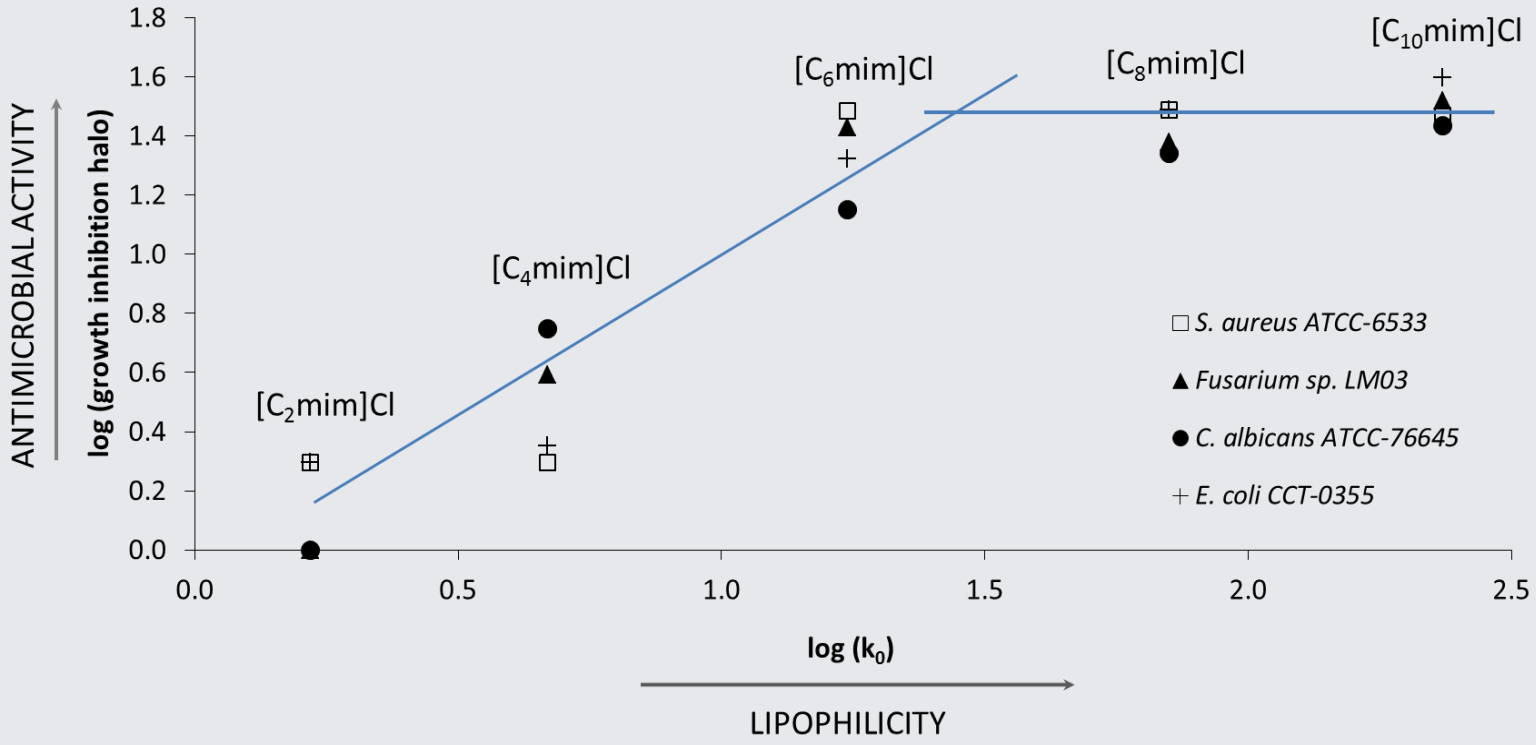
Ionic Liquids



Solvation of alcohols in ILs



Antimicrobial activity



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CHEMISTRY
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Full Paper

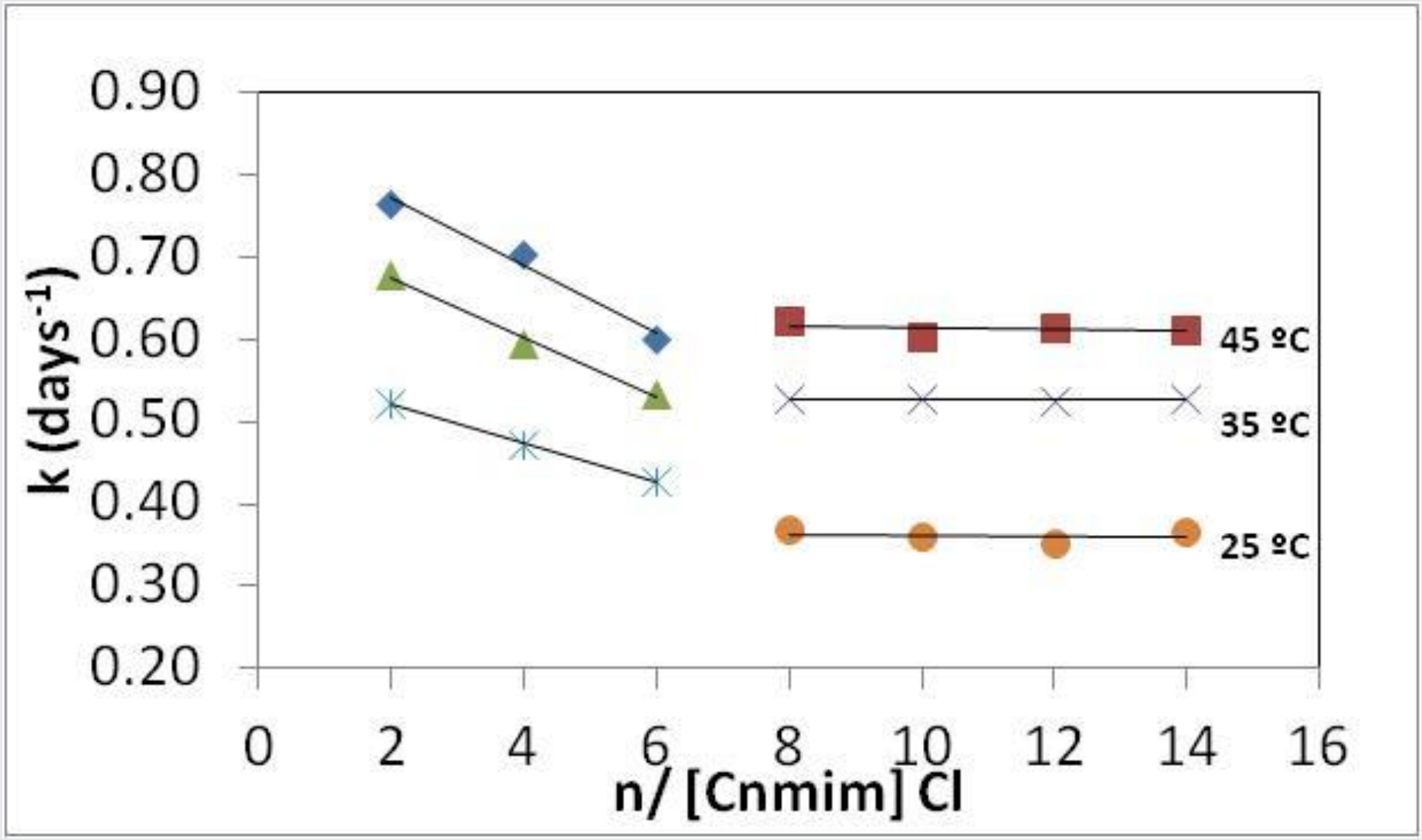
Ionophores

Molecular Parameters and Transmembrane Transport Mechanism of Imidazolium-Functionalized Binols

Marc Vidal and Andreea Schmitzer*[a]

Abstract: We describe the molecular parameters governing the transmembrane activity of imidazolium-functionalized anion transporters and present a detailed mechanistic study. These ionophores adopt a mobile-carrier mechanism for short methyl and butyl chains, a combined mobile-carrier/transmembrane-pore mechanism for octyl and dodecyl chains, and form transmembrane aggregates for hexadecyl chains.

Laccase: Thermal stability



Lipase superactivity

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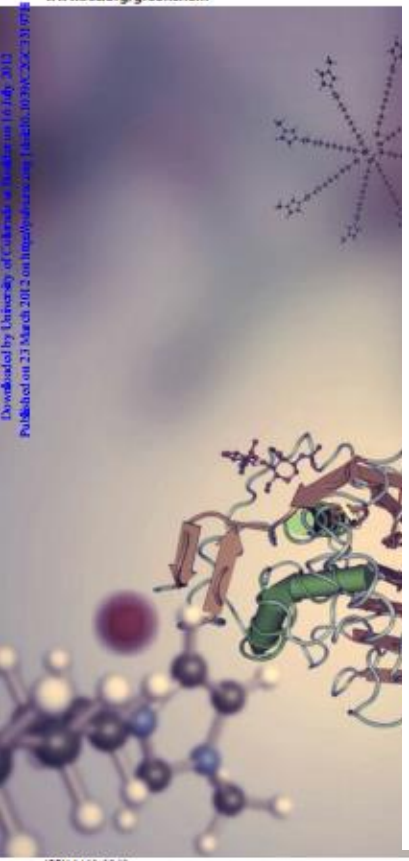

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1463-9262 (2012) 14:6;1-P

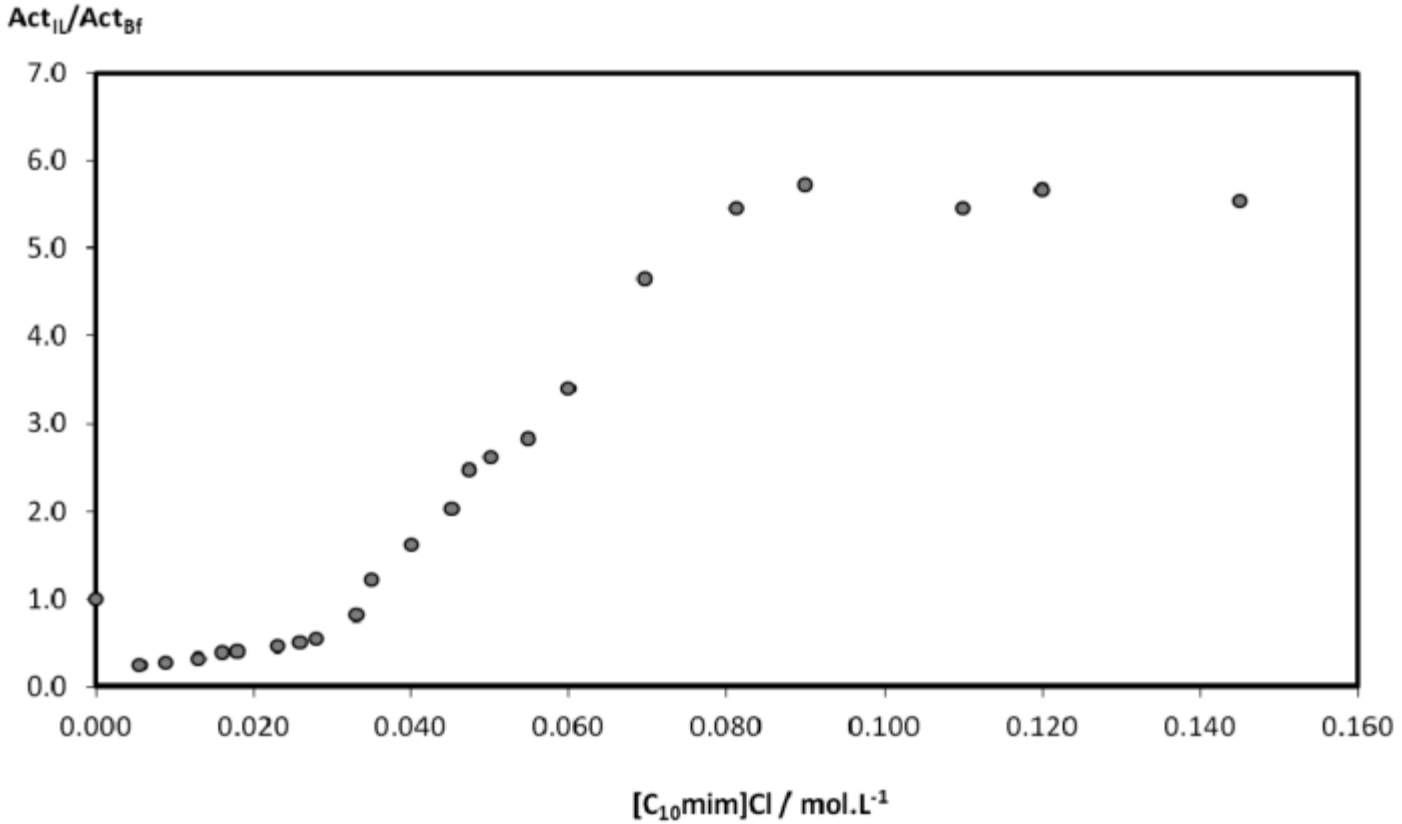
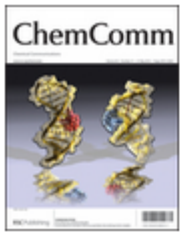


Fig. 1 The relative enzyme activity of CaLB as a function of the concentration of $[C_{10}mim]Cl$.

Micellar catalysis



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Micellar catalysis in aqueous–ionic liquid systems

Katharina Bica,*[a] Peter Gärtner,[a] Philipp J. Gritsch,[a]

Anna K. Ressmann,[a] Christian Schröder[b] and Ronald Zirbs[c]

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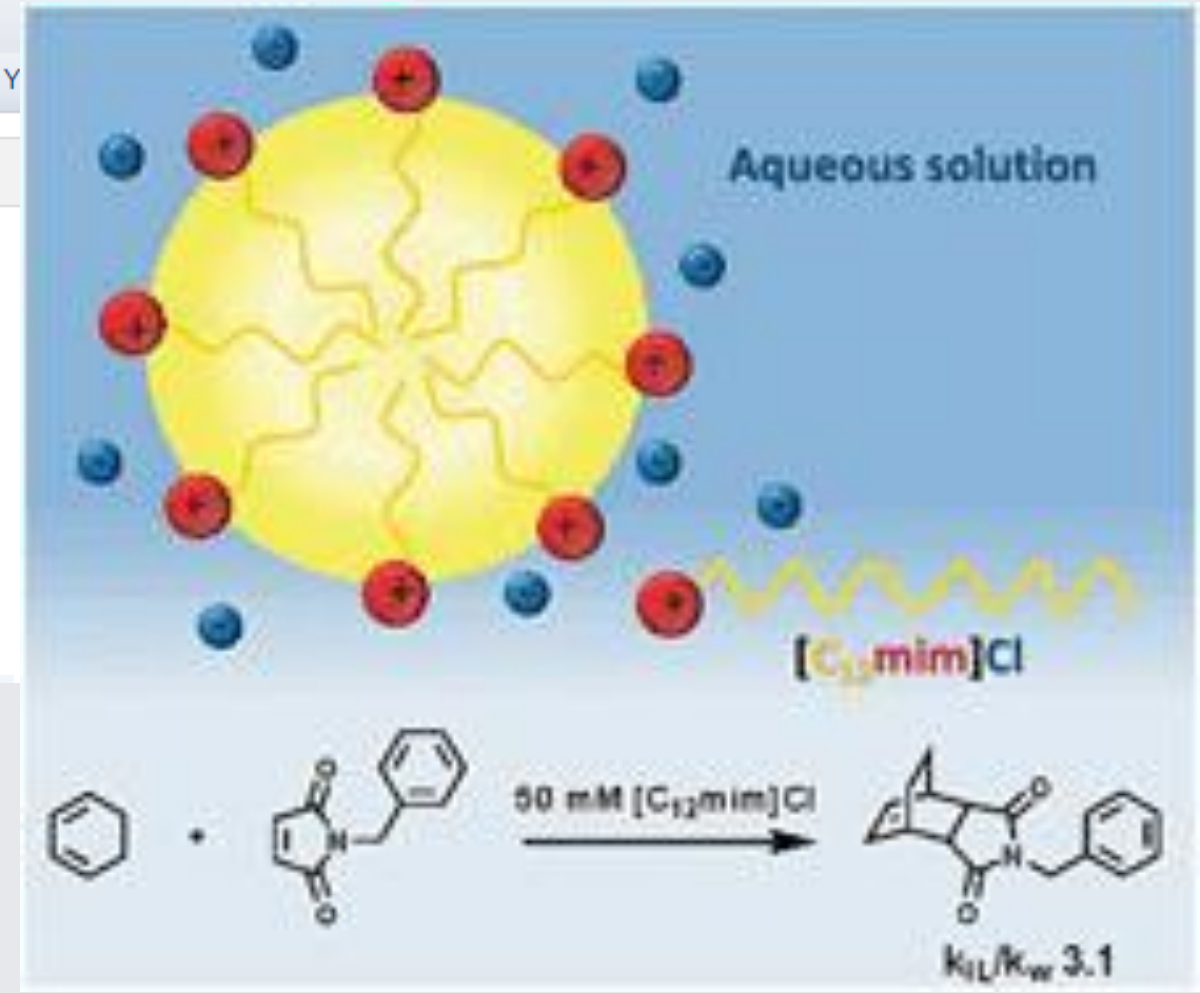
First published online 28 Mar 2012



ThermPhys

Working Group

Thermophysical Properties of Solids and Fluids

Path (path.web.ua.pt)

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