Transport Properties in Ionic Liquids

Update and Challenges

COST 1206 - EXIL workshop, Carlos Nieto de Castro
Prague, April 21st-22nd, 2015 cacastro@ciencias.ulisboa.pt

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Objective

- To analyse the evolution in the last decade in the thermophysical properties of IL's, from experiment to methods of calculating thermophysical properties (correlation, prediction estimation).
- We will try in this paper to **select the current challenges for ionic liquids**, especially focussed in the understanding of their properties and its use in problem solving in the area of sustainable chemistry.

How can we obtain Thermophysical Property Data?

- Literature
- Data Banks, Correlations
- Direct Experimental Determination (very limited and time consuming)
- Models and Computer Simulation
- Prediction/Estimation

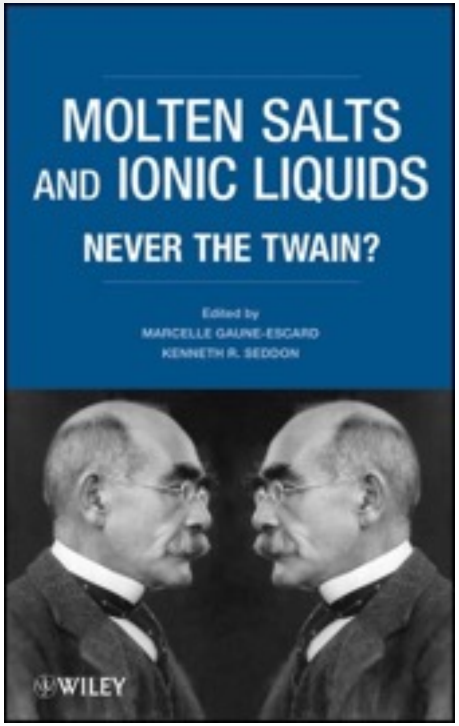
Problem

- The high rate of data needed, **especially for new systems and compounds**, led to the development of "friendly user" measuring equipments, of data bases and interactive routines prepared for the design of these items (black boxes), and many estimation schemes for properties have been implemented
- Unfortunately, in most cases, they **do not pay attention** to the **accuracy** of the experimental data or the **prediction/estimation techniques** that form the basis of the algorithms involved

Why?

- There are several reasons:
  - Calculations based only on empirical bases, not taking into account the quality of the experimental data used
  - No validation / quality control of proposed methods (rigorous critical assessment of data)
  - Generalization of the applications to molecular different systems – models non-applicable
  - Wrong correlations, bad interpolations and worse extrapolations

MEASURING TRANSPORT PROPERTIES OF IONIC LIQUIDS



ISBN: 978-0-471-77392-4
441 pages
April 2010

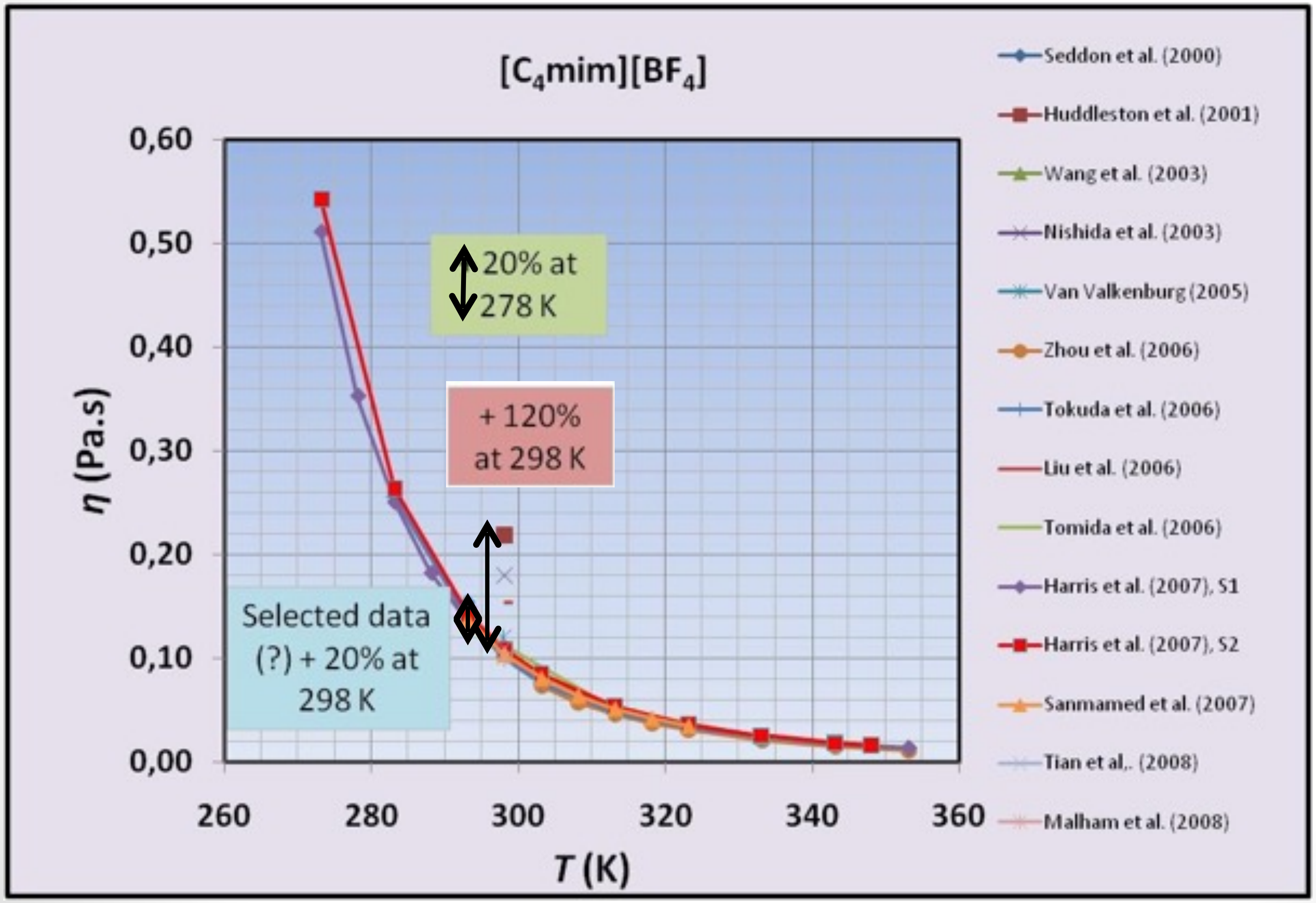
Chap 17 **Accurate Measurement of Physicochemical Properties on Ionic Liquids and Molten Salts**
V. M. B. NUNES, M. J. V. LOURENÇO, F. J. V. SANTOS, M. L. S. M. LOPES, and
C. A. NIETO DE CASTRO
Presented at EUCHEM 2006, Hammamet, Tunisia

Topics discussed in this volume include structure, dynamics, electrochemistry, interfacial and thermodynamic properties, spectroscopy, synthesis, and theoretical studies. Experimental and theoretical methods for investigating these data are elaborated, as are techniques for data collection and analysis. **This book represents the first serious discussion on the transfer of these methods and techniques between the differing temperature regimes, and is a major contribution to the future of both fields.**

There we wrote

- *Even for molecular liquids, where the interactions in the liquid state are essentially known and easier to characterize, it is still difficult to measure properties with high accuracy*
- ***Ionic liquids, made of isolated or aggregated ions, are electrically conducting, polarizable, and almost nonvolatile, posing several problems for the design and use of standard equipments***

One Example – Viscosity of [C_4mim][BF_4] - (Data up to 2008 - ILTHERMO)



20% at 278 K

+ 120% at 298 K

Selected data (?) + 20% at 298 K

What can affect the measurements?

- **Sample**
  - Preparation
  - Handling
  - Characterization (impurities, structure)
- **Chemical reactivity**
- **Mathematical modeling of the instrumentation used**

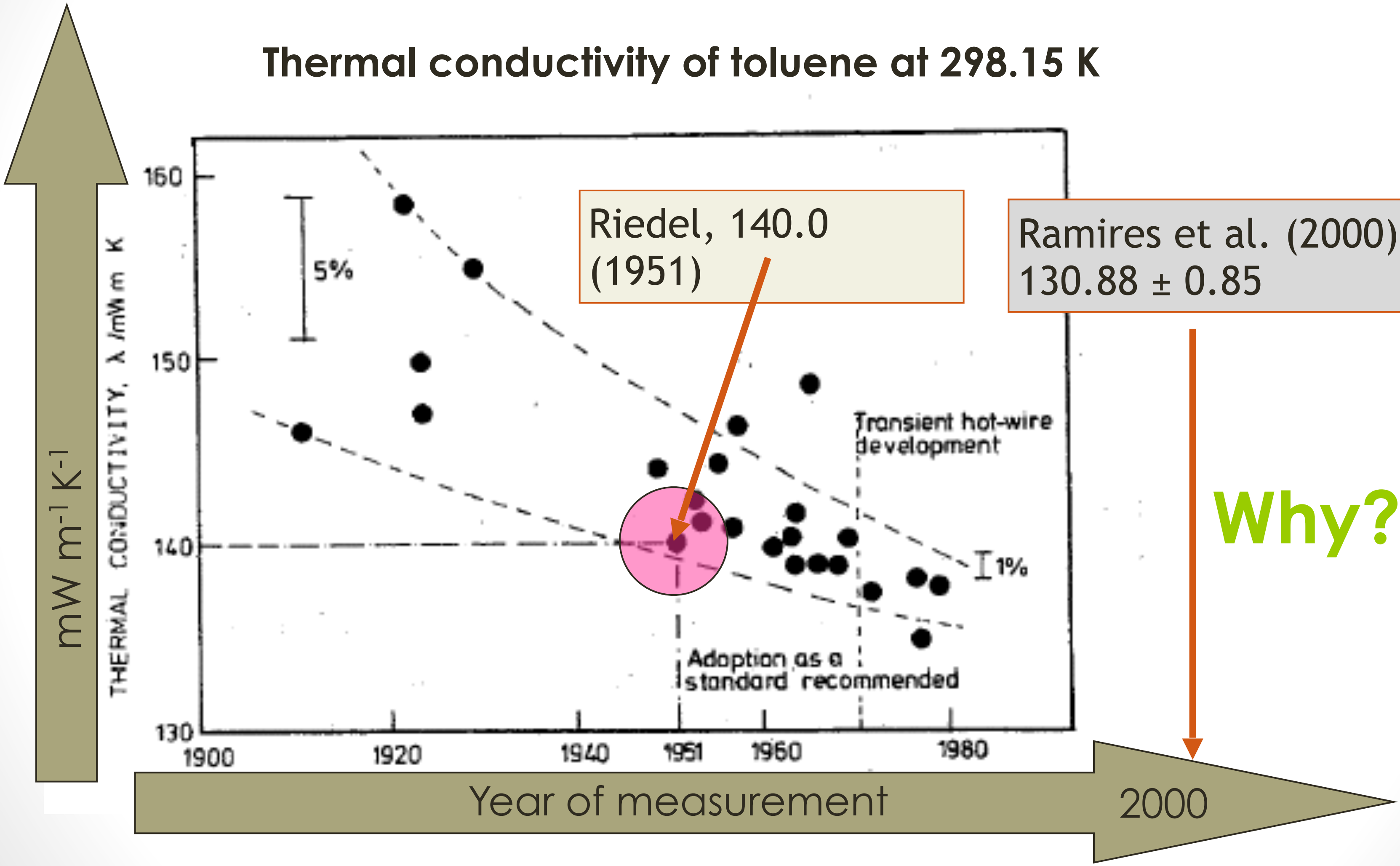
- *Invited Talk at 17th STP, Boulder, 2009*

And…

- Measurement of the thermophysical properties (thermodynamic and especially transport) is done in many laboratories, **not always with the best qualification** for the/ method of measurement and procedure to be used
- The use of available instrumentation (commercial), without a careful consideration of ionic liquid properties, **can constitute a serious bad contribution to data bases and process designers**

- *Invited Talk at 17th STP, Boulder, 2009*

Is this problem new? NO!



Thermal conductivity of toluene at 298.15 K

Riedel, 140.0 (1951)

Ramires et al. (2000) 130.88 ± 0.85

Why?

Illustration with **Viscosity** measurement methods

- No primary methods
- "quasi-primary" - any method for which a physically sound working equation, relating the viscosity to the experimental-measured parameters, is available, but where some of these parameters must be obtained accurately by an independent calibration with a known standard
  - Oscillating body (disk, cup, cylinder and sphere)
  - Vibrating wire
  - Torsional oscillating quartz crystal
  - Surface light scattering spectroscopy (SLS)

- The data obtained with these state-of-the-art instruments have smaller uncertainties (or greater accuracies), when compared with data obtained using other **secondary methods (calibration needed)**, namely the capillary viscometer (in any of its versions), the rolling-ball viscometer or the falling ball viscometer, **whose calibration parameters do not possess a clear physical meaning**

Applicability of existing methods to ILs

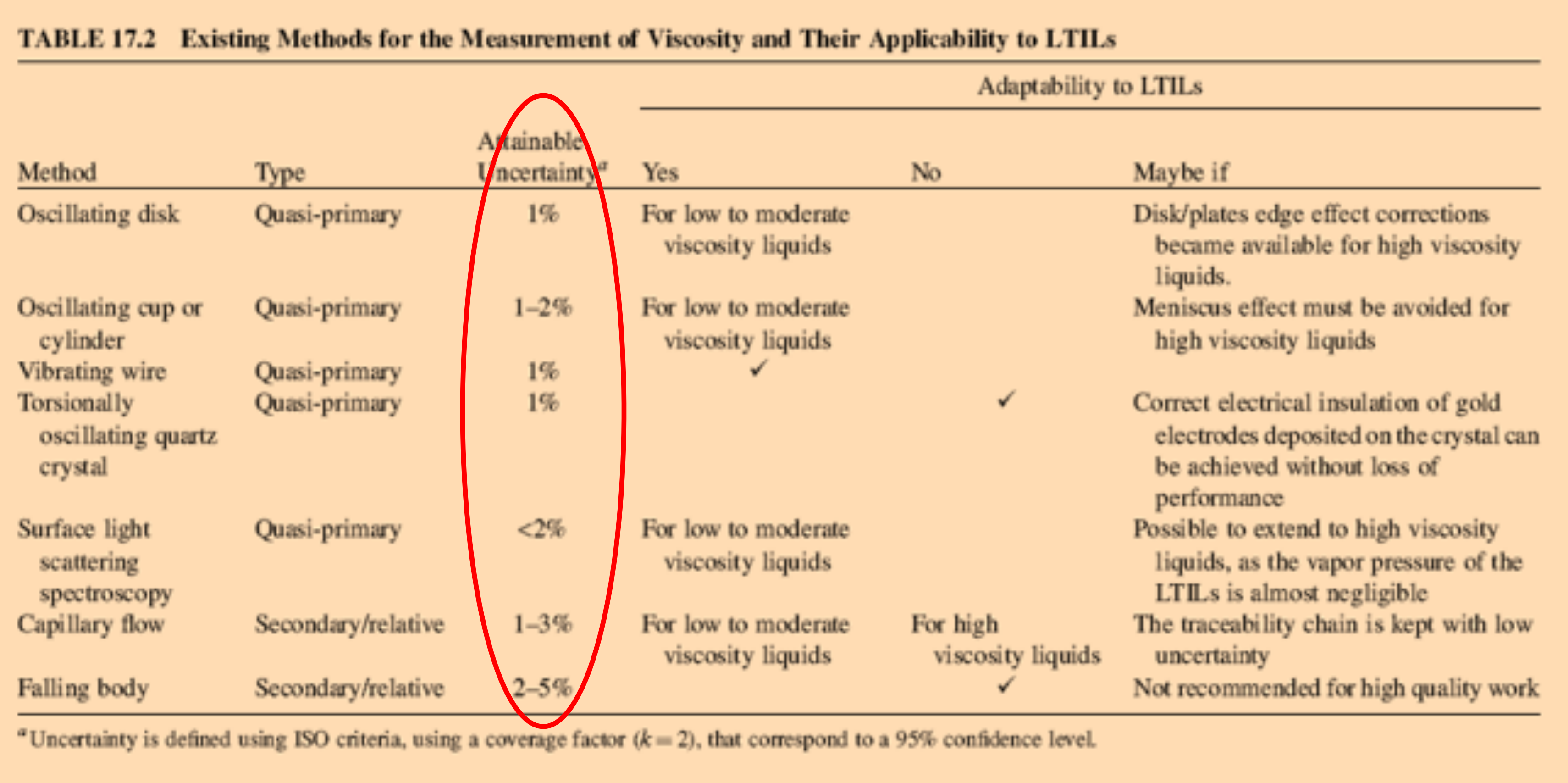


TABLE 17.2 Existing Methods for the Measurement of Viscosity and Their Applicability to LTILs

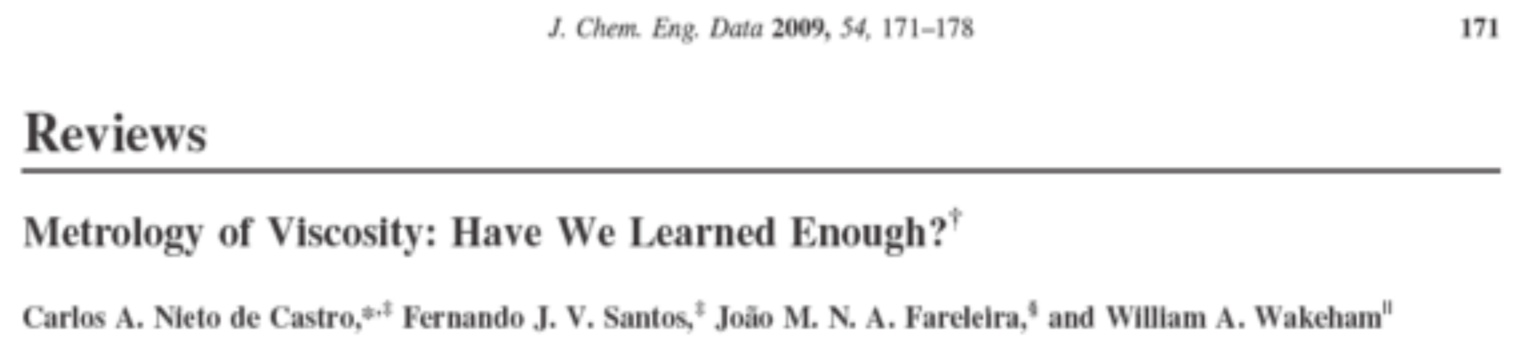
Method	Type	Attainable Uncertainty[a]	Adaptability to LTILs: Yes	No	Maybe if
Oscillating disk	Quasi-primary	1%	For low to moderate viscosity liquids		Disk/plates edge effect corrections became available for high viscosity liquids.
Oscillating cup or cylinder	Quasi-primary	1–2%	For low to moderate viscosity liquids		Meniscus effect must be avoided for high viscosity liquids
Vibrating wire	Quasi-primary	1%	✓		
Torsionally oscillating quartz crystal	Quasi-primary	1%		✓	Correct electrical insulation of gold electrodes deposited on the crystal can be achieved without loss of performance
Surface light scattering spectroscopy	Quasi-primary	<2%	For low to moderate viscosity liquids		Possible to extend to high viscosity liquids, as the vapor pressure of the LTILs is almost negligible
Capillary flow	Secondary/relative	1–3%	For low to moderate viscosity liquids	For high viscosity liquids	The traceability chain is kept with low uncertainty
Falling body	Secondary/relative	2–5%		✓	Not recommended for high quality work

[a] Uncertainty is defined using ISO criteria, using a coverage factor ($k = 2$), that correspond to a 95% confidence level.

Also used: Stabinger /rotating concentric cylinders – uncertainty estimated to 3-5 %

Please Read…

2009


J. Chem. Eng. Data 2009, 54, 171–178

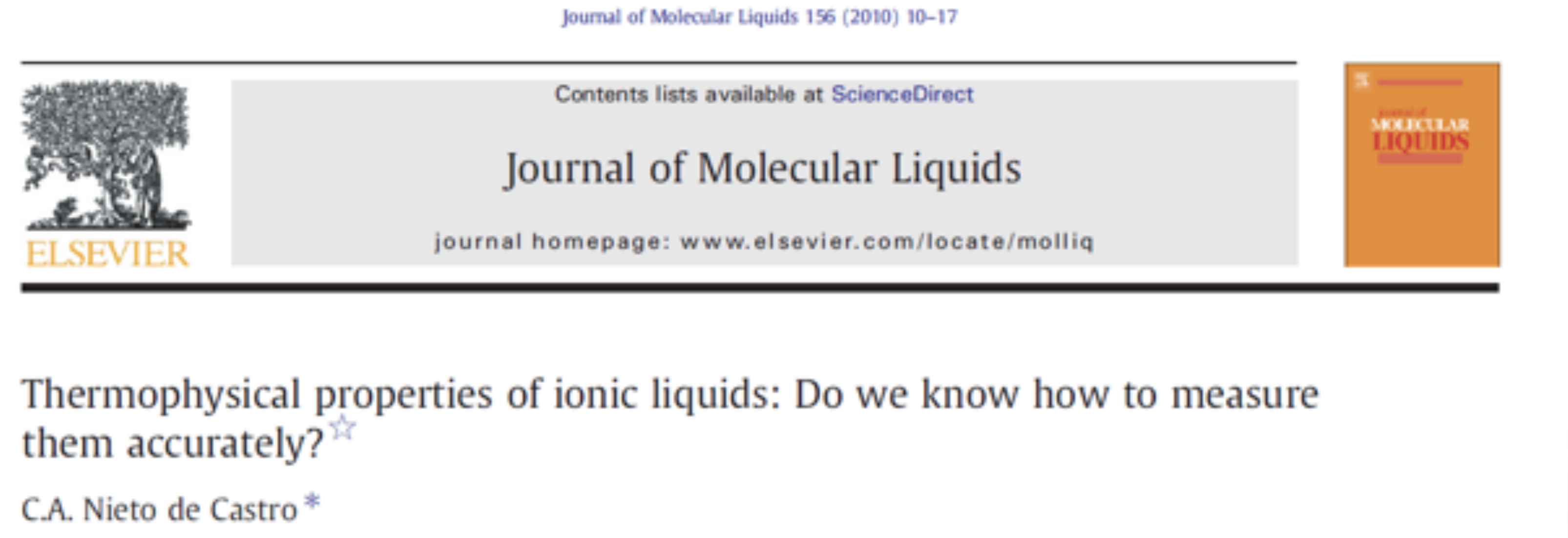
171

Reviews

Metrology of Viscosity: Have We Learned Enough?[†]

Carlos A. Nieto de Castro,[*,‡] **Fernando J. V. Santos,**[‡] **João M. N. A. Fareleira,**[§] **and William A. Wakeham**[∥]

2010


Journal of Molecular Liquids 156 (2010) 10–17

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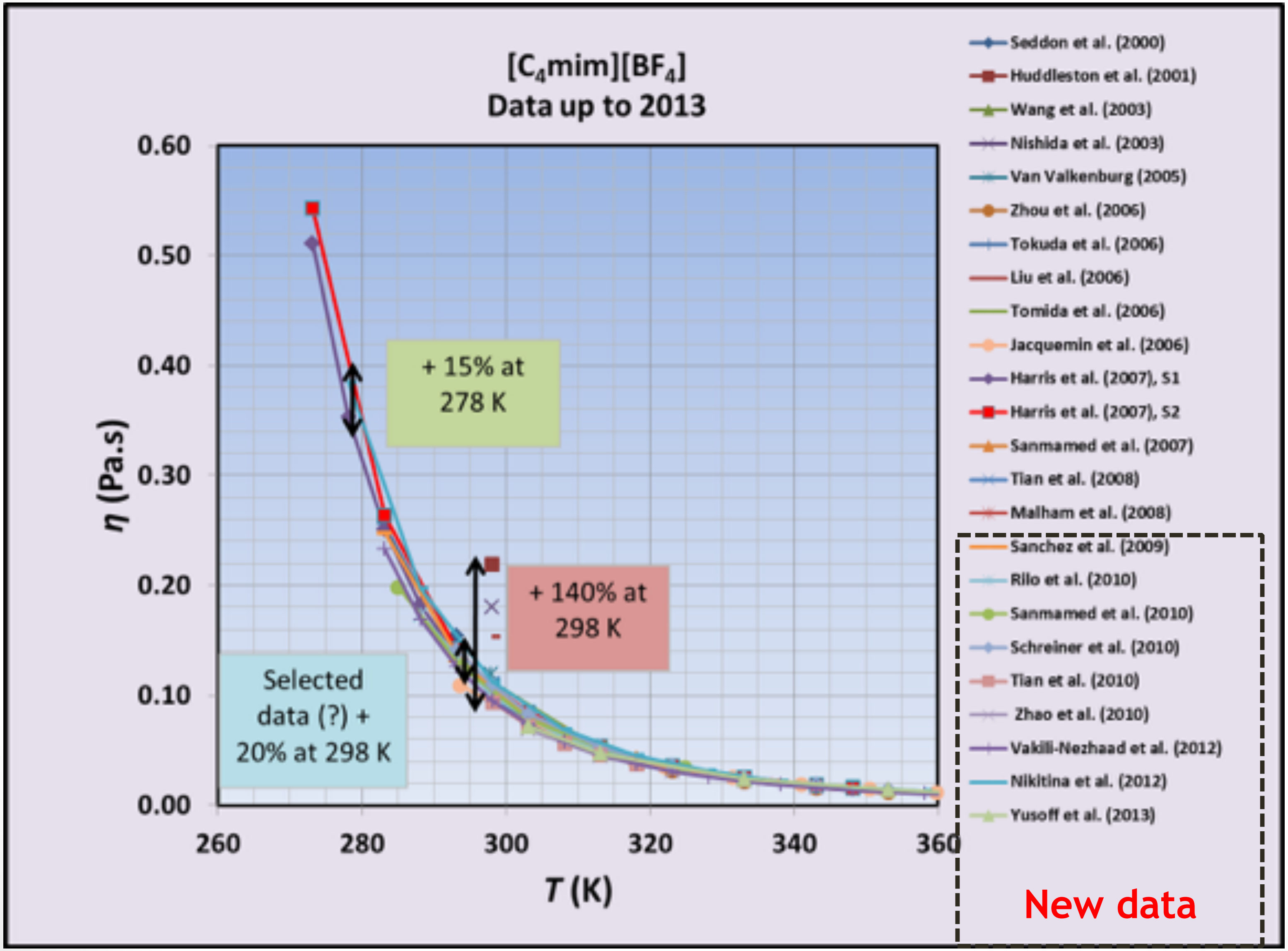
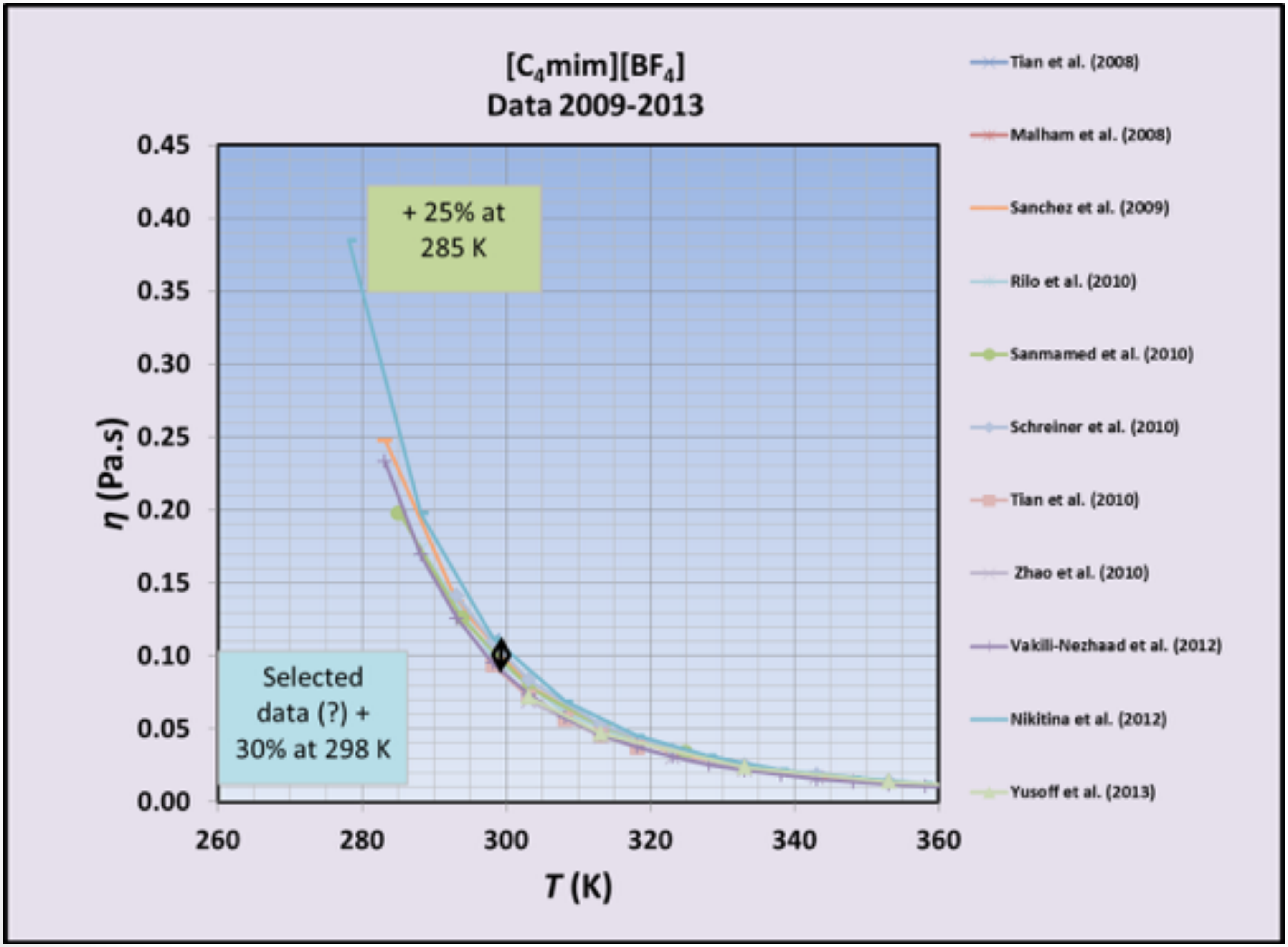
Thermophysical properties of ionic liquids: Do we know how to measure them accurately?☆

C.A. Nieto de Castro *

Same IL – Data up to 2013 (ILTHERMO) Better?



Same IL – Data 2009 to 2013 (ILTHERMO)



$[C_4mim][BF_4]$
Data 2009-2013

+ 25% at 285 K

Selected data (?) + 30% at 298 K

And…

- The scatter of data is even bigger - 140% (all data) at 300 K! But if we use only data after 2008 it does improve – only 30%
- People just measures but do not take account of the quality of the measurement
- People do not read fundamental papers, just has to publish …
- Impurities (halide ions, Na^+, other IL's, left solvents, etc…)
- Water?
- Method of measurement, not applicable?

And if we know how to measure?... At least some of us!

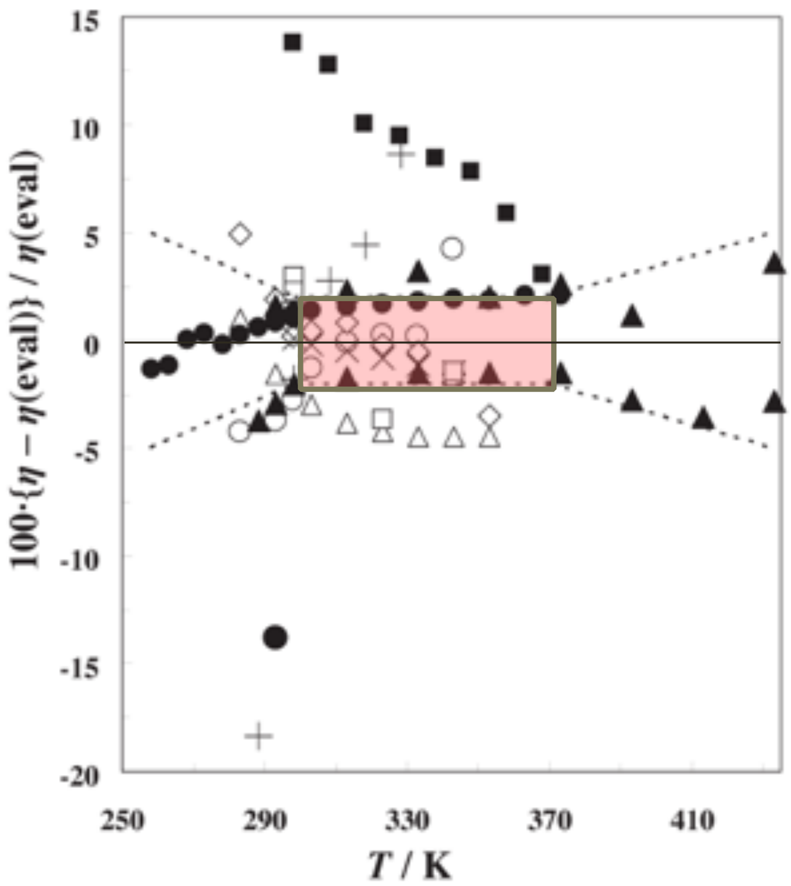


Fig. 8 Deviation plot for experimental viscosities η from the critically evaluated va
4 for [C_6mim][NTf_2] near pressure p = 0.1 MPa. The IUPAC sample was studied by: ▲, Kandil et al. [22]; ×, Santos et al. [35]; ●, Widegren and Magee [4]; ■, Seddon and Driver [24]. Non-IUPAC samples were studied by: ●, Fitchett et al. [26]; ○, Crosthwaite et al. [16]; △, Tokuda et al. [17]; ◇, Tokuda et al. [32]; □, Ahosseini and Scurto [36]; +, Mohammad et al. [33]. The dashed lines represent the combined expanded uncertainties for η(eval).

$[C_6mim][(CF_3SO_2)_2N]$

Viscosity (near pressure *P* = 0.1 MPa)

± 2% , for 293 to 373 K

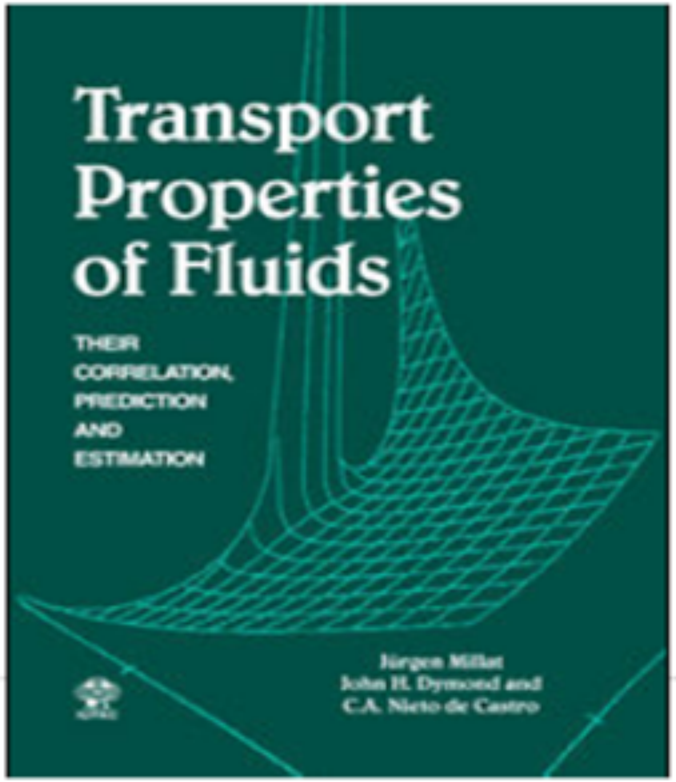
Viscometers used:

- **Vibrating wire**
- **Stabinger**
- **Capillary**

BUT....Deviations (-16 to + 16)% from IUPAC correlation (PAC 2010)

Good agreement?

- Samples from the same batch of synthesis, purified
- Characterized by ^{1}H and ^{19}F NMR (purity greater than 99.5%) (0.998 in fact)
- Water content (before and after the measurements) determined by Coulometric Karl-Fisher titration
- Standard procedures for handling the sample to minimize contamination with water



Transport Properties of Fluids

THEIR CORRELATION, PREDICTION AND ESTIMATION

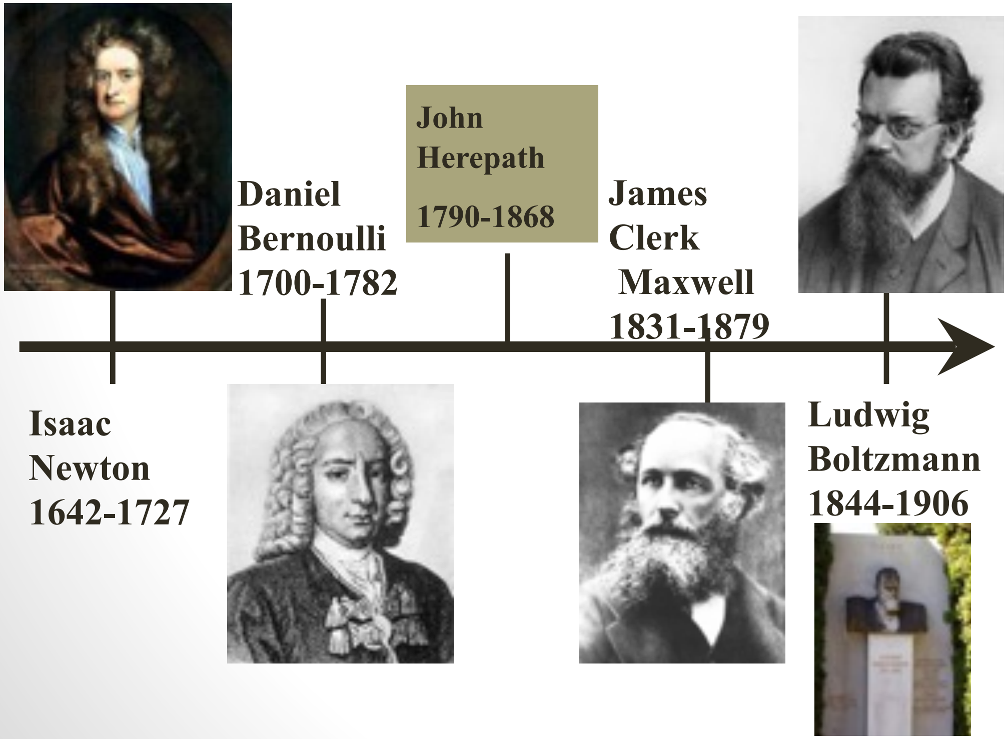
Jürgen Millat
John H. Dymond and
C.A. Nieto de Castro

Prediction, Estimation ….What works!

METHODS OF CALCULATING PROPERTIES

Molecular Basis of Property Calculations

- ➢Kinetic theory of gases
- ➢Statistical thermodynamics



Isaac
Newton
1642-1727

Daniel
Bernoulli
1700-1782

John
Herepath
1790-1868

James
Clerk
Maxwell
1831-1879

Ludwig
Boltzmann
1844-1906

➢**Johannes Diderik van der Waals** (1837-1923), **Rudolf Clausius** (1822-1888) and **James Prescott Joule** (1818-1889)

➢1880-1930 - **Gibbs, Enskog e Chapman**

➢**Wang-Chang e Uhlenbeck** in 1953

Their work made possible:

- Theoretical result of the **equation of state of gases** (until then empirical),
- The first expressions for **the viscosity of a gas**,
- The understanding of the **concept of real gas**, and therefore, of the equation of van der Waals and the virial equation (namely the second virial coefficient
- The concept of **molecular energies** (translational, rotational, vibracional, electronic)
- The first expression for the **heat capacity of gases**, after the appearance of Quantum Mechanics

Fundamental

Johanes Diderik van der Waals
(1837-1923)

- Nobel Prize for Physics in 1910, "*for the work on the equation of state for gases and liquids*"
- Continuity between the gaseous and liquid states and the explanation for the critical point
- First equation of state for a real gas

Result

- For the first time **it was possible to compare results obtained empirically** (determined on the laboratory) **with theoretically based calculations** (statistical mechanics + model of interaction potential) for very simple systems
- In the years 1960’s, 1970’s and 1980’s these approaches have been extended to more complex systems, introducing in the models different “quantity” of empirical information

Classes of Property Calculation

- Prediction
  - Semi theoretical prediction
  - Prediction methods and models
- Estimation
  - Semi-theoretical estimation
  - Approximate theoretical methods
  - Semi-empirical estimation
  - Empirical estimation

Predictive/Estimation Methods for IL's – Main Difficulties

- Predictive/Estimation methods are a fundamental tool to be developed, to be incorporated in Process Design Simulators
- However, due to our current understanding at a nano-dimension, the existing intermolecular forces and the supporting theories, **it is extremely difficult to develop theoretical based predictive schemes**
  - The number of combinations of cations and anions is immense, ~10^{18}
  - The structure of the cations and anions varies very much
  - Generalizations are difficult

Conclusion

- ➢Even if we now understand the structure of IL's in the liquid state, we cannot yet calculate properties, except by modelling the interactions and performing molecular dynamics experiments.
- ➢But it has to be dealt, system by system – impossible generalizations!

Can we use traditional Methodology for Ionic Liquids?

- A series of methods that enable the calculation of transport properties, have to be developed, based on:
  - approximate solutions of the fundamental equations
  - **on heuristic extensions of the theory (Van der Waals model, free volume theory)**
  - **or on totally empirical information**, like the behaviour of a given property for a group of structural similar compounds - **group contribution methods**
  - **Pure estimation methods**

Correlations

- Careful correlation of accurate experimental data gives reliable values at **interpolated** temperatures and pressures (densities), at different compositions
- Careful! **Not all the experimental measurements deserve the same reliability**
- Unfortunately, there are only a limited number of systems where data of such accuracy are available
- Moreover, **for engineering purposes**, there is seldom available the data needed for a particular new design, specially for multicomponent mixtures
- If the correlation is not based, or at least inspired, in molecular theory, **we can not extrapolate**!

WE ARE LEFT WITH ESTIMATION TECHNIQUES …

… USUALLY BASED ON CORRELATIONS

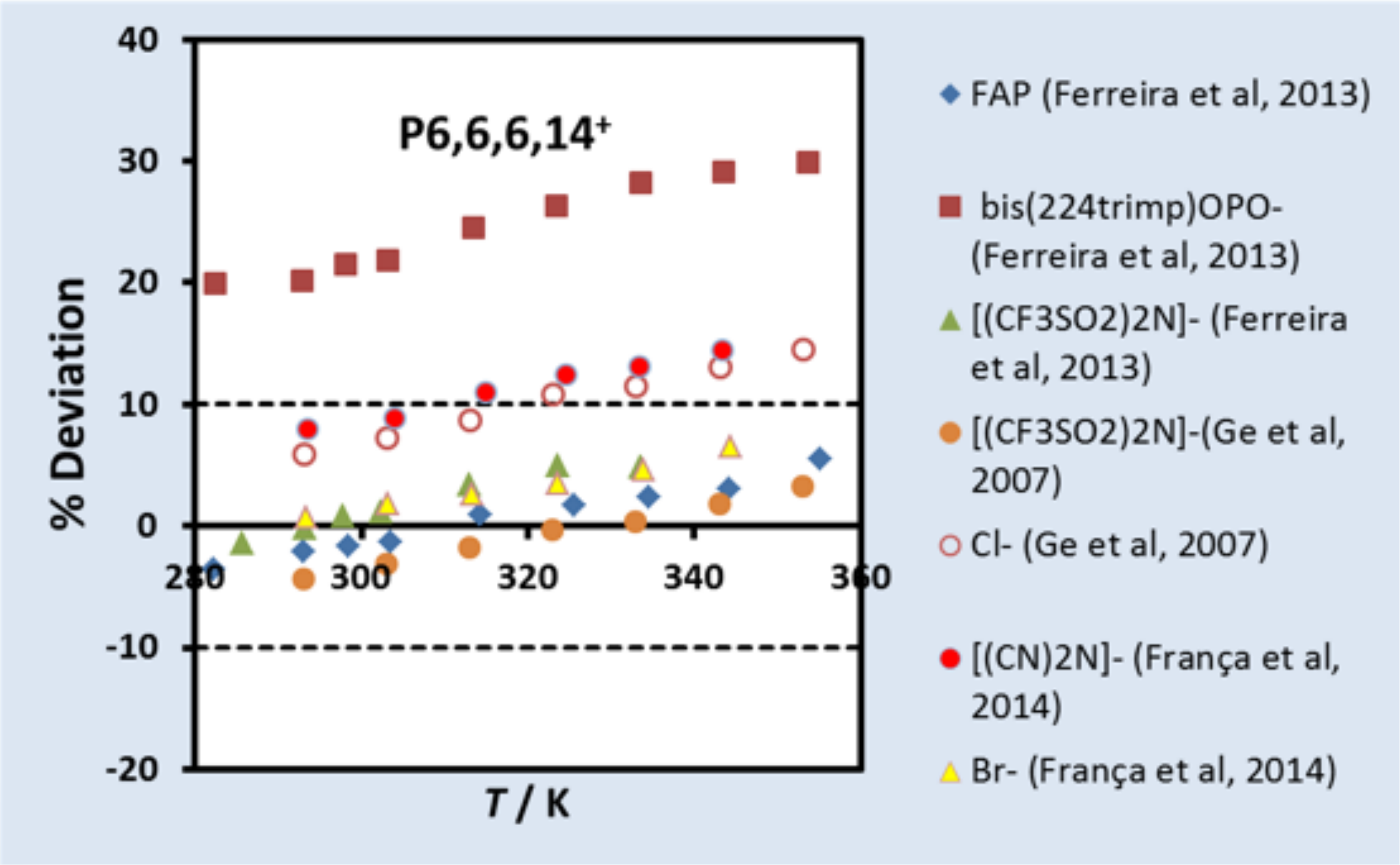
Thermal Conductivity of Pure IL’s

EXAMPLE

Available methods

- Heuristic extensions of the theory (Van der Waals model) – see papers by Maciño et al., Int. J. Thermophys. **35**, 812-829, 2014
- **Purely empirical methods**
    - Mohanty relationship (Tomida et al)
    - Fröba 's methods (extended by Ferreira et al) (2010,2014)
    - Group contribution methods, Coutinho's group (2007-2009) and Wu et al. (2013)
    - Albert and Muller (2014)

Ferreira et al. (2013)



Fröba et al. (2014)

T.M. Koller, S.R. Schmid, S.J. Sachnov, M.H. Rausch, P. Wasserscheid, A.P. Fröba, "Measurement and Prediction of the Thermal Conductivity of Tricyanomethanide and Tatetracyanoborate Based IL's" Int J Thermophys (2014) 35:195–217

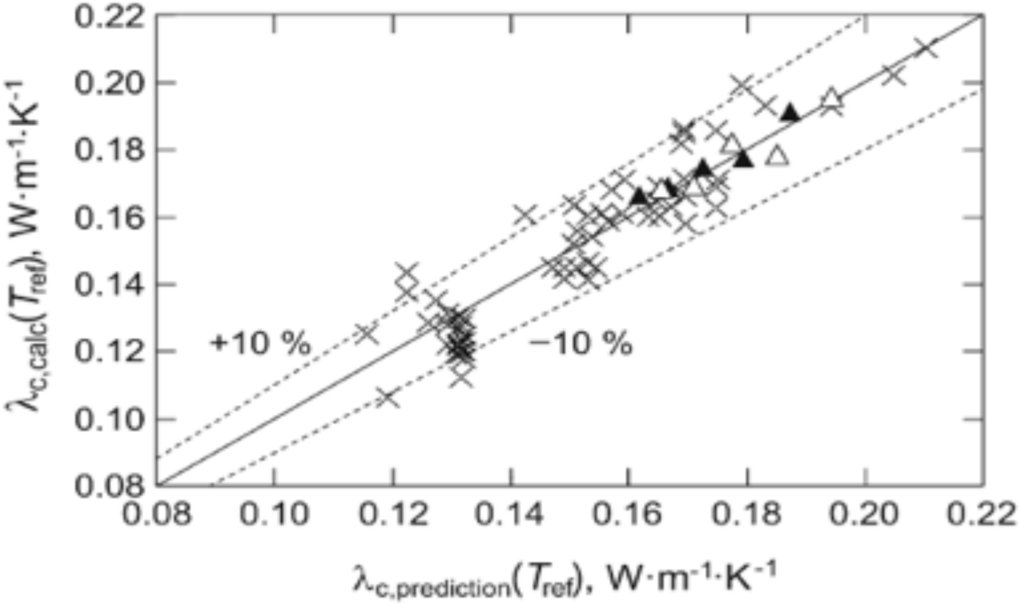


Fig. 3 Comparison of thermal conductivity $\lambda_{c,calc}(T_{ref})$ calculated using Eq. 5 with thermal conductivity $\lambda_{c,prediction}(T_{ref})$ predicted using Eq. 7 with $A = 0.0960\,\mathrm{W\cdot m^{-1}\cdot K^{-1}}$ and $B = 21.43\,\mathrm{g^2\cdot cm^{-3}\cdot W\cdot m^{-1}\cdot K^{-1}\cdot mol^{-1}}$ at $T_{ref} = 293.15\,\mathrm{K}$: △, $[\mathrm{C(CN)_3}]$-based ILs; ▲, $[\mathrm{B(CN)_4}]$-based ILs; ×, literature data [5,6,8,10–19]. The dashed lines indicate relative deviations of $\lambda_{c,calc}(T_{ref})$ from $\lambda_{c,prediction}(T_{ref})$ of −10 % and +10 %

$$\lambda_{c,prediction}(T_{ref}) M \rho_{calc}(T_{ref}) = A M \rho_{calc}(T_{ref}) + B$$

[C(CN)3]⁻ and [B(CN)4]⁻ based IL's

$$\lambda_{c,prediction}(T) = \lambda_{c,calc}(T_{ref}) \left(\frac{\rho_{calc}(T)}{\rho_{calc}(T_{ref})} \right)^{C}.$$

$C = 0.826$

Albert and Muller (2014)

8%?

$$\lambda_{\mathrm{estimation}} = (A_{\mathrm{cation}} + A_{\mathrm{anion}}) - (B_{\mathrm{cation}} + B_{\mathrm{anion}}) \cdot T$$

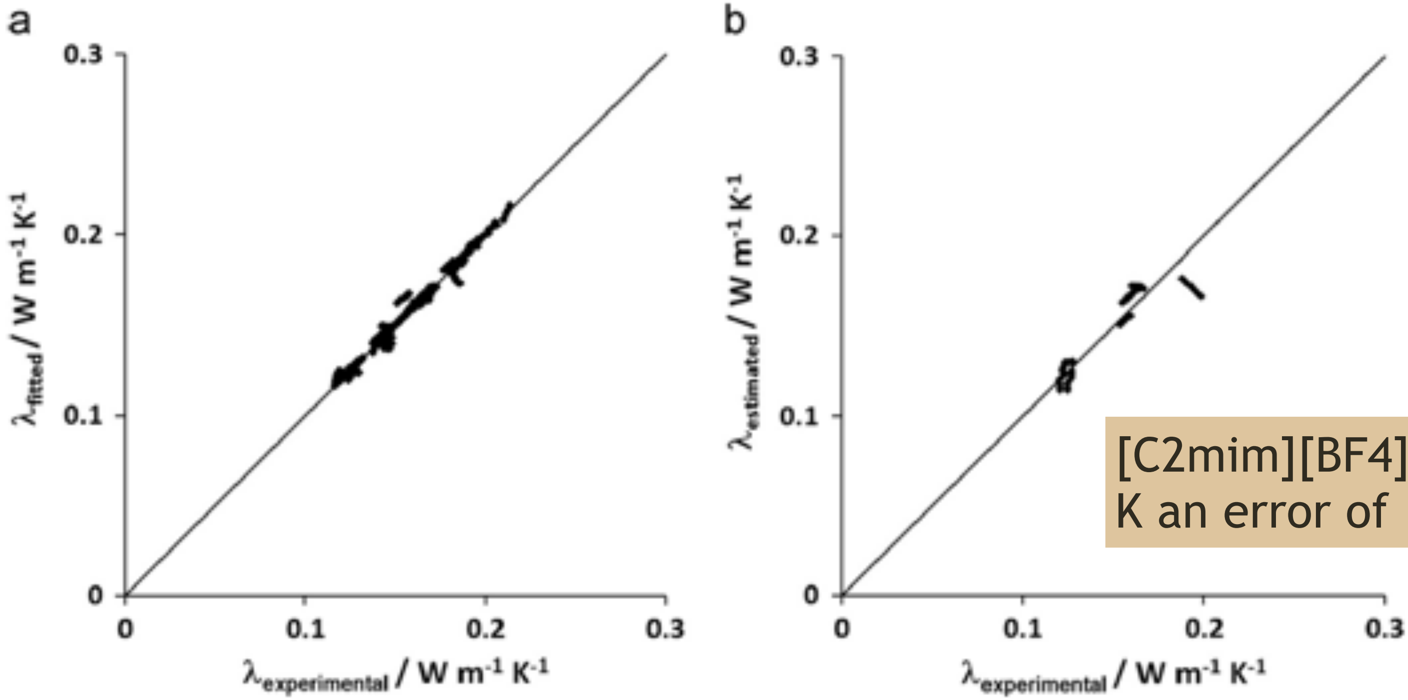


Fig. 3. Estimated values plotted over the experimental values for the training set (a) and for the test set (b).

[C2mim][BF4] at 300 K an error of 19.4%!

Chemical Engineering Science 119 (2014) 109–113

Idea – Using simple models

- Free-Volume/Hole Theory or Eyring schemes for viscosity and Bridgman model for thermal conductivity
- Viscosity of a dense phase has two contributions (far from critical points)

Dilute phase   Dense phase

$$\eta = \eta_0 + \Delta\eta$$

H. E. Quinteros-Lama, Carlos A. Nieto de Castro, H. Segurat, to be published

Needs – EOS, adjustable
Needs 3 adjustable parameters – L_0, α, B - correlation

Quiñones-Cisneros, S. E.; Deiters, U. K. J. Phys. Chem. B 2006, 110, 12820–12834

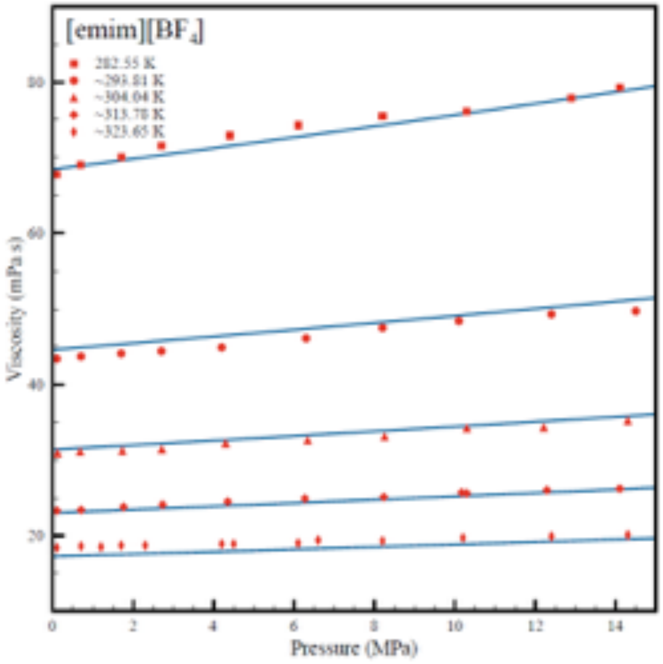
For the exemplification of the methodology of Free-Volume correlation, the EOS - PC-SAFT equation of state was used

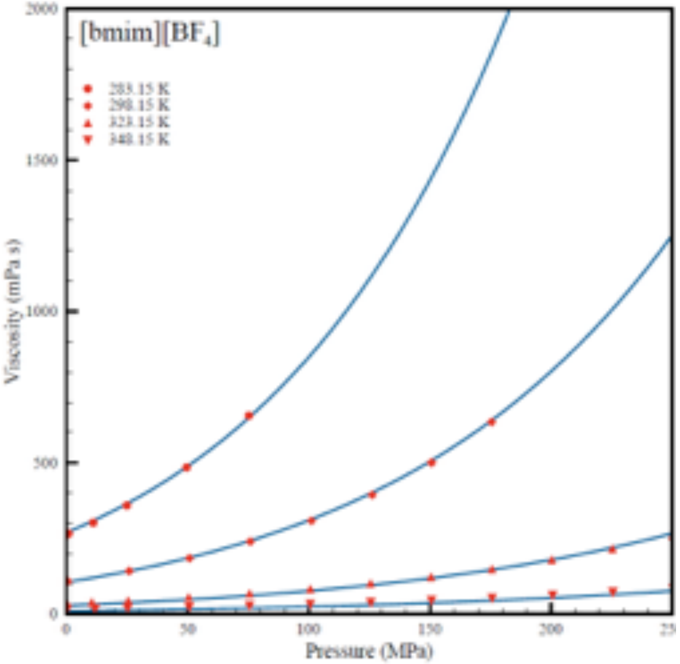
$$\Delta\eta = \prod_1^3 \eta_i$$

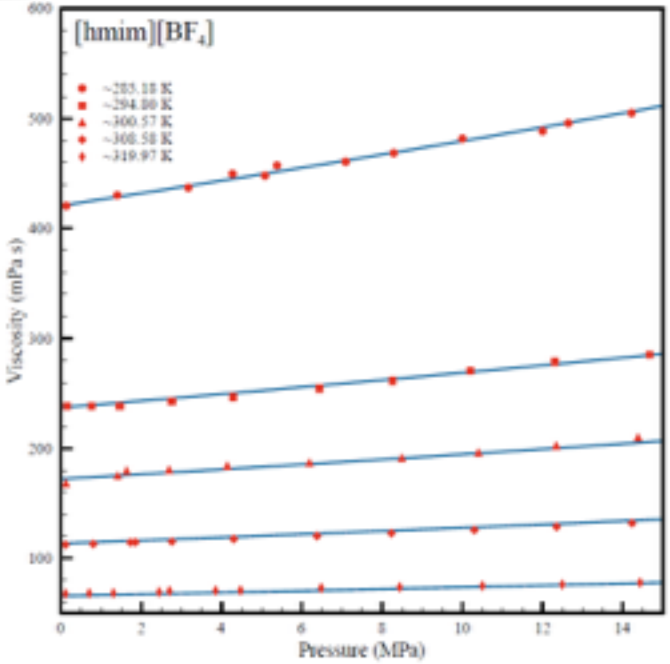
$$\eta_1 = L_0 L_v\left(\alpha\rho^2 M_w - \tilde{A}_v\right)$$

$$\eta_2 = \left(\frac{M_w}{3\phi_1 RT}\right)^{1/2}$$

$$\mathbf{ln}\,\eta_2 = B\left(\frac{-\tilde{A}_v + \alpha\rho^2 M_w}{\rho RT}\right)^{3/2}$$



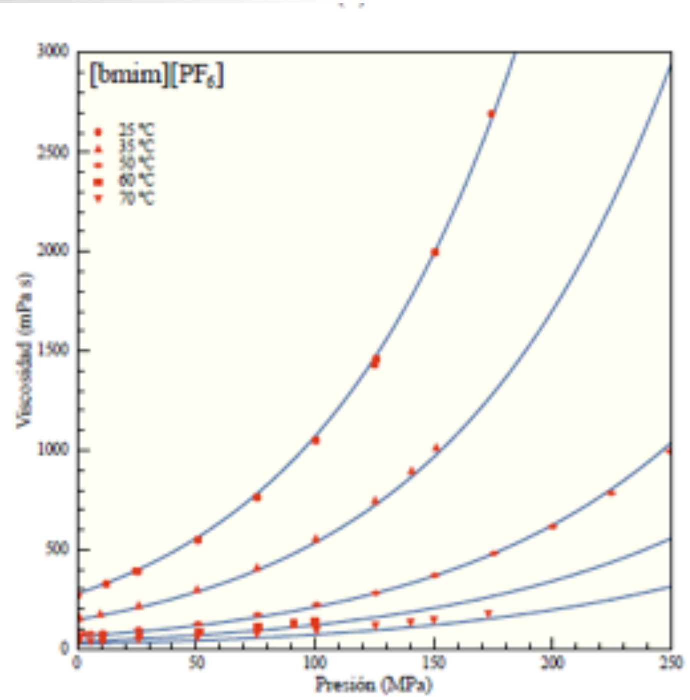


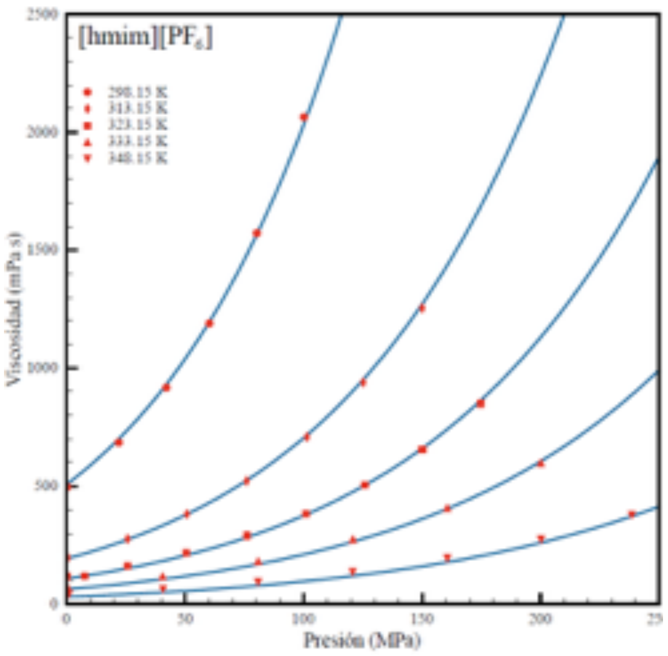


$[C_nmim][BF_4]$

Fitting is very promising…

Model is real! Trends are predicted by simple theory!





[C$_n$mim][PF$_6$]

Excellent agreement!
Can we extrapolate – NO!
Can we interpolate - YES

Please Note

- The correlation is independent of the equation of state used for volume
- Table shows the AAD predicted with PC-SAFT and soft-SAFT for the same set of experimental data of IL of $[BF_4]$ family.

	PC-SAFT	soft-SAFT*
$[C_2mim][BF_4]$	**2.46**	**8.80**
$[C_3mim][BF_4]$	**4.53**	**5.13**
$[C_4mim][BF_4]$	**9.50**	**5.80**
$[C_6mim][BF_4]$	**3.46**	**6.29**
$[C_8mim][BF_4]$	**6.76**	**7.42**
Average	**5.94**	**6.69**

*F.L. Llovell, L.F. Vega, Assessing Ionic Liquids Experimental Data Using Molecular Modelling: $[C_nmim][BF_4]$ Case Study, JCED. 59 (2014) 3220–3231

Thermal Conductivity

- Equation of Bridgman + PC-SAFT.
- 1 Adjustable parameter α

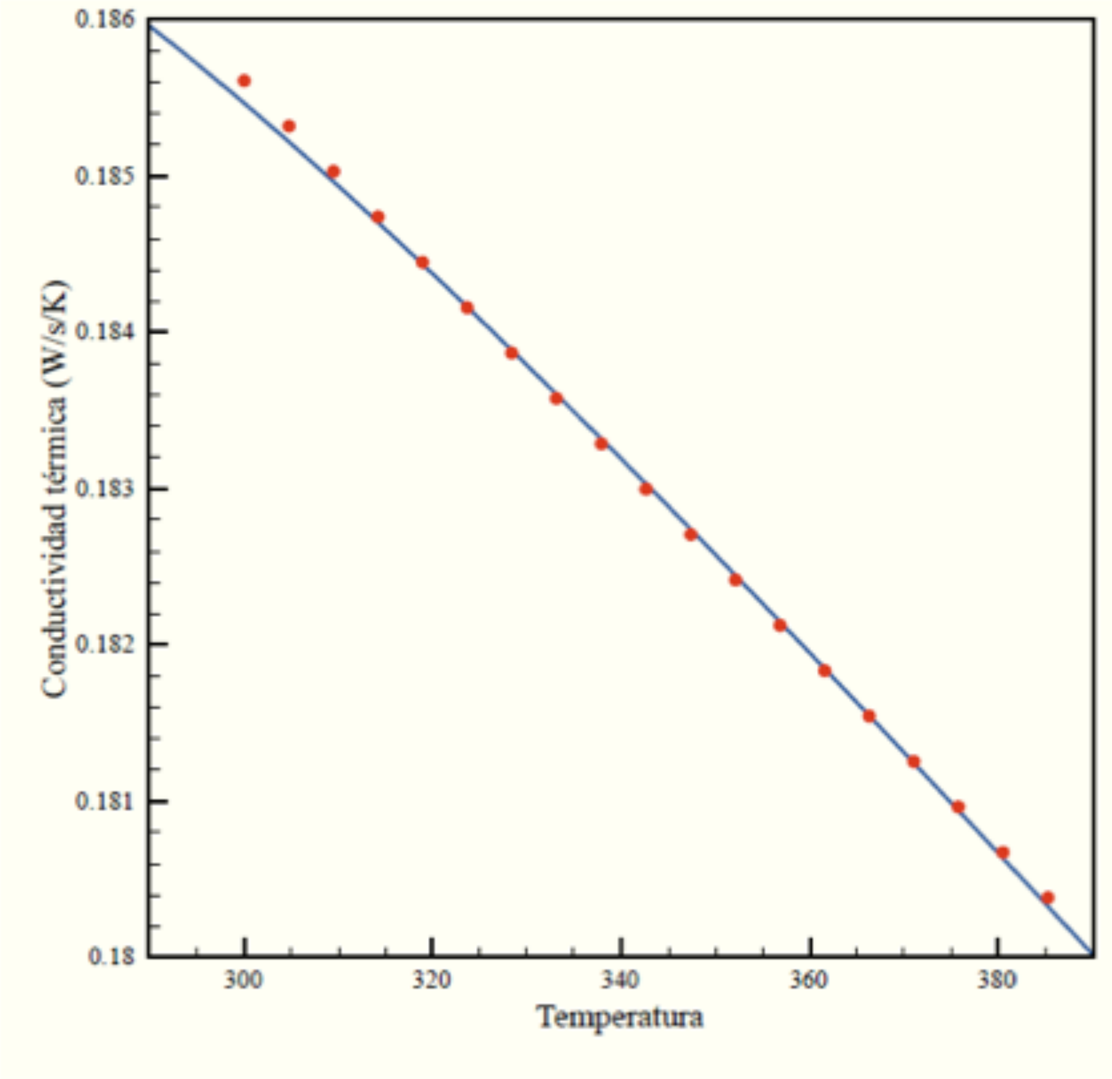
$$\lambda = \rho \tilde{C}_v u a$$

$$a = \left(\frac{V}{N}\right)^{1/3} \approx k_0 \tilde{v}^{1/3} = k_0 \left(\frac{M_w}{\rho}\right)^{1/3}$$

$$\lambda = k_0 \rho^{2/3} \tilde{C}_v u M_w^{1/3}$$

$$\lambda = \frac{\alpha}{M_w^{1/6}} \frac{T}{\tilde{v}^{5/6} \tilde{A}_{2v} \tilde{A}_{2T}^{1/2}} \left(\tilde{A}_{2T} \tilde{A}_{2v} - \tilde{A}_{vT}^2\right)^{3/2}$$

$[C_4mim][BF_4]$



M.E.V. Valkenburg, R.L. Vaughn, M. Williams, J.S. Wilkes, Thermochemistry of ionic liquid heat-transfer fluids, Thermochim. Acta. 425 (2005) 181–188.

But…

Valkenburg et al. data is ~ 13 % higher than our measurements!

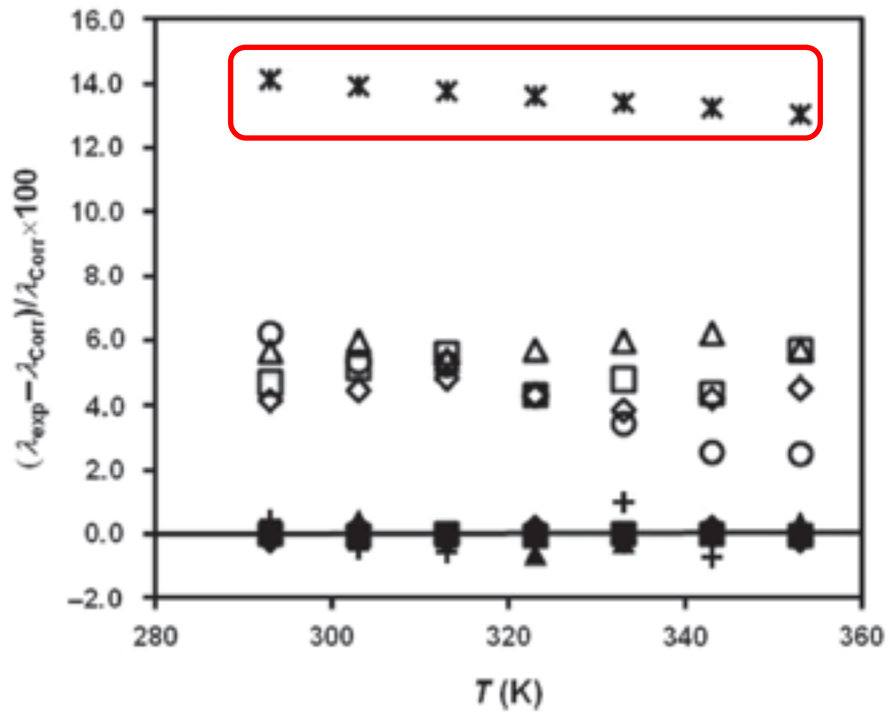


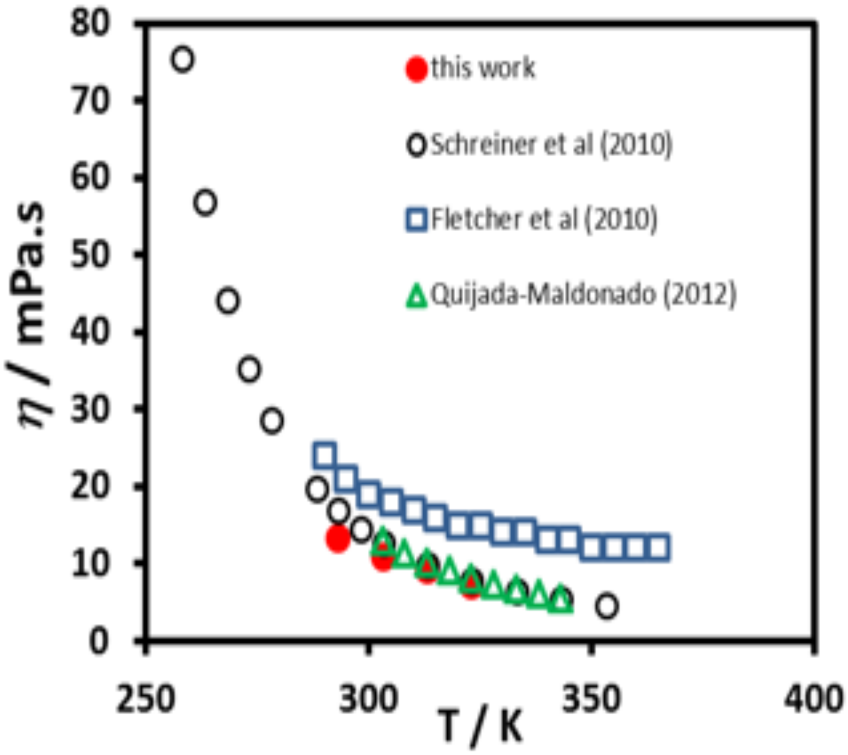
Fig. 2. Deviations between our data and other data from Eq. (1), as a function of temperature. ●—$[C_2mim][(CF_3SO_2)_2N]$; +—$[C_4mim][(CF_3SO_2)_2N]$; ▲—$[C_6mim][(CF_3SO_2)_2N]$; ◆—$[C_8mim][(CF_3SO_2)_2N]$; ■—$[C_4mim][BF_4]$; Δ—$[C_2mim][(CF_3SO_2)_2N]$;[17] ○—$[C_4mim][(CF_3SO_2)_2N]$;[17] ◊—$[C_6mim][(CF_3SO_2)_2N]$;[17] □—$[C_8mim][(CF_3SO_2)_2N]$;[17] ∗—$[C_4mim][BF_4]$.[19]

A.P.C. Ribeiro, S.I.C. Vieira, P. Goodrich, C. Hardacre, M.J.V. Lourenço, C.A. Nieto de Castro, “Thermal conductivity of $[C_nmim][(CF_3SO_2)_2N]$ and **$[C_4mim][BF_4]$** IoNanofluids with carbon nanotubes – Measurement, theory and structural characterization”, J. Nanofluids 2, 55–62 (2013).

Estimation?

- Extensive analysis has to be done, to be able to include more ions
- But experimental data is still necessary, as there are still quite a lot of discrepancies.
- Example – viscosity of $[C_2mim][dca]$

$[C_2mim][dca]$



Which data should we choose to develop the estimation method?

Conclusions

- ➢From the challenges of IL’s applications (mostly related chemistry and chemical engineering) within many areas to the complexity of inter and intramolecular interactions between the ions and third species (other ions, molecular solvents or nanomaterials), **there is a wide range of quality research still to be performed**
- ➢**Transport properties (heat capacity, thermal conductivity, viscosity) and other thermophysical properties play an important role in the applications**

Recommendations - Experimental

- Characterize very well the sample
- Decide if the instrument you have is adequate for IL’s
- Especially for viscosity, avoid moisture when handling and filling the cells
- Demonstrate that the ILs are Newtonian
- Calculate accurately the uncertainty of the measurement – do not be exceeding optimist
- If using secondary methods, use SRD and calibrants of high quality, namely for **high viscosity** (250 – 1000 mPa.s)

Conclusions - Modelling

- Our present knowledge of the structure of ionic liquids and about the real balance of all intermolecular forces is still deficient
- **Modelling is fundamental in this phase, as well as computer simulations in real systems**
- Van der Walls model, Free-volume/ Eyring model and group contribution methods are the best alternatives at the moment for thermophysical property estimation (some correlations needs adjustment with better experimental data).
- For thermal conductivity, the equation of Bridgman seems promising
- Need to extend to mixtures of IL's with H_2O, CO_2 and NH_3

What Must Be Our Attitude?

- **First:** Base our calculations in the **Molecular Theory** (molecular thermodynamics and kinetic theory of gases and liquids), when available
- **Second:** Only generalize with solid physical and chemical grounds
- **Third:** When experimental data is necessary, **use only the best (higher accuracy)** existing
- **Fourth:** Validate the calculations with critical comparisons with experiments

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SEVENTH FRAMEWORK PROGRAMME

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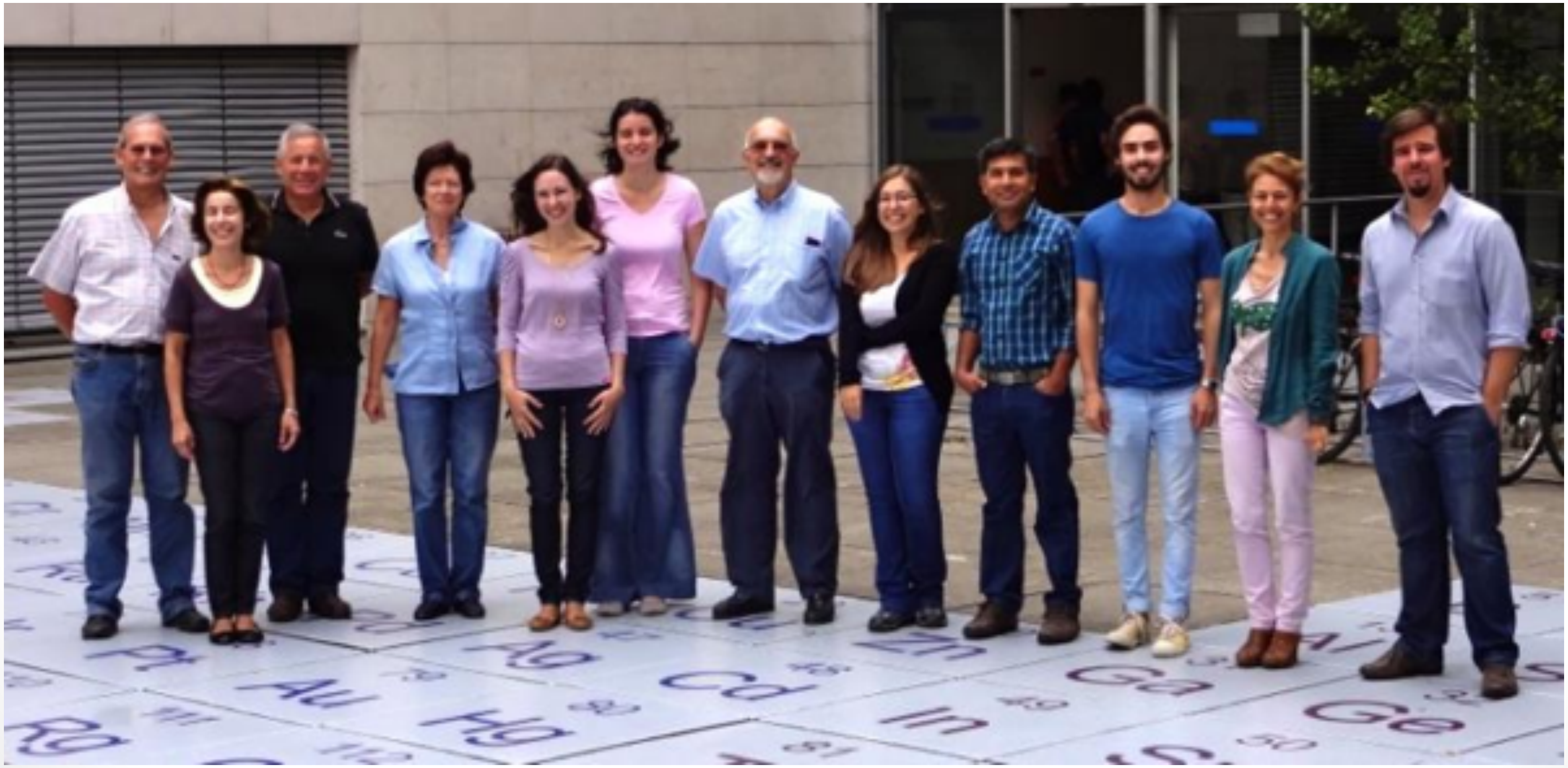
NARILAR

Molecular Thermophysics and Fluid Technology Group



- Many projects are undergoing

- Students (MSc, PhD), Post-Docs
- WELCOME!

- Contact cacastro@ciencias.ulisboa.pt
- Condition: To love Ionic Liquids, Nanomaterials or Engineering Fluids!

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