Development of a Solubility Parameters Scale for Ionic Liquids

Marta Batista

Orientado por:
João A. P. Coutinho

universidade de aveiro

Summary

- **Introduction**
  - Biofuels
  - Ionic Liquids
  - Solubility Parameter
- **Estimation of the Solubility Parameter**
  - Activity coefficients at infinite dilution
  - Viscosity
- **Experimental Section**
- **Conclusion**
- **Future work**
- **Acknowlegdements**

Introduction

▸ Bioethanol and Biobutanol – Work context

Bioethanol & Biobutanol

- ❖ Reneawable resources
- ❖ Liquid transport fuels replacing the usual fuels
- ❖ Reduce emissions of hydrocarbon, carbon monoxide
- ❖ Improves the engine combustion

Introduction

Bioethanol and Biobutanol

- The production of biofuels by *fermentation* requires a process for the *recovery of alcohol from the aqueous medium*

DISTILLATION

The presence of water will form an azeotrope with the alcohol

Introduction

Extractive Distillation – Problem Resolution

- Azeotropic distillation
- Liquid-liquid extraction
- Pervaporation
- **Extractive distillation**

Third component added to the mixture – Change in the relative volatility of compounds

- organic solvent
- solid salt
- mixture
- **IONIC LIQUID**

Introduction

▸ Extractive Distillation with Ionic Liquids

IL as entrainer

- Breaking of azeotropes
- Less energy consumption
- Lower costs
- Lower capital investment

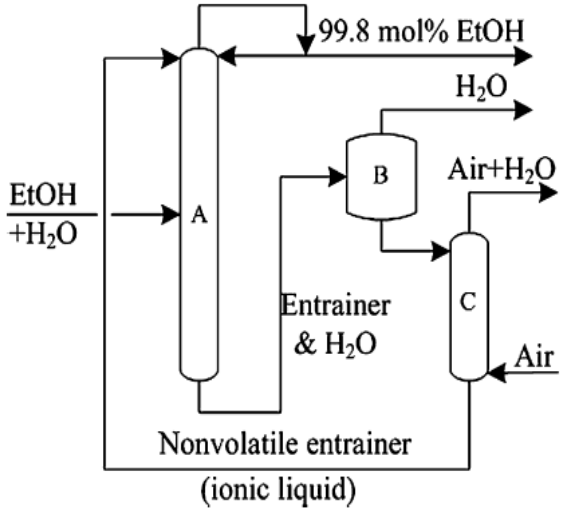
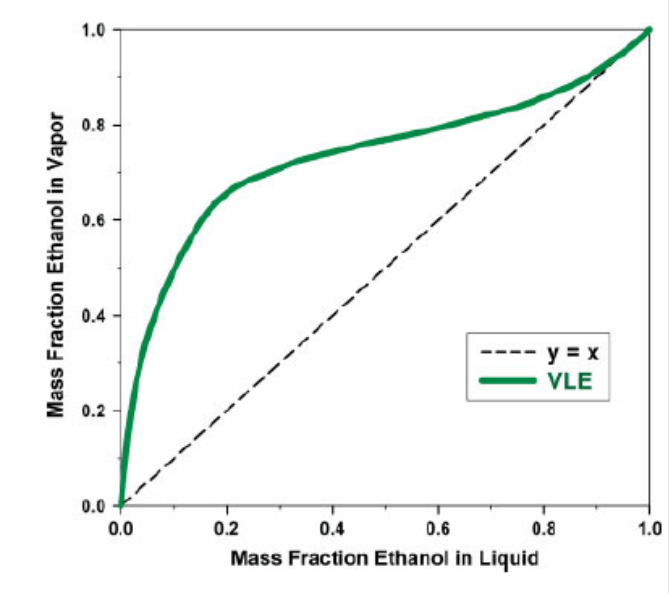


Fig. 14. Extractive distillation using ionic liquid as non-volatile entrainer (A: main column, B: flash drum, C: stripping column) [93].

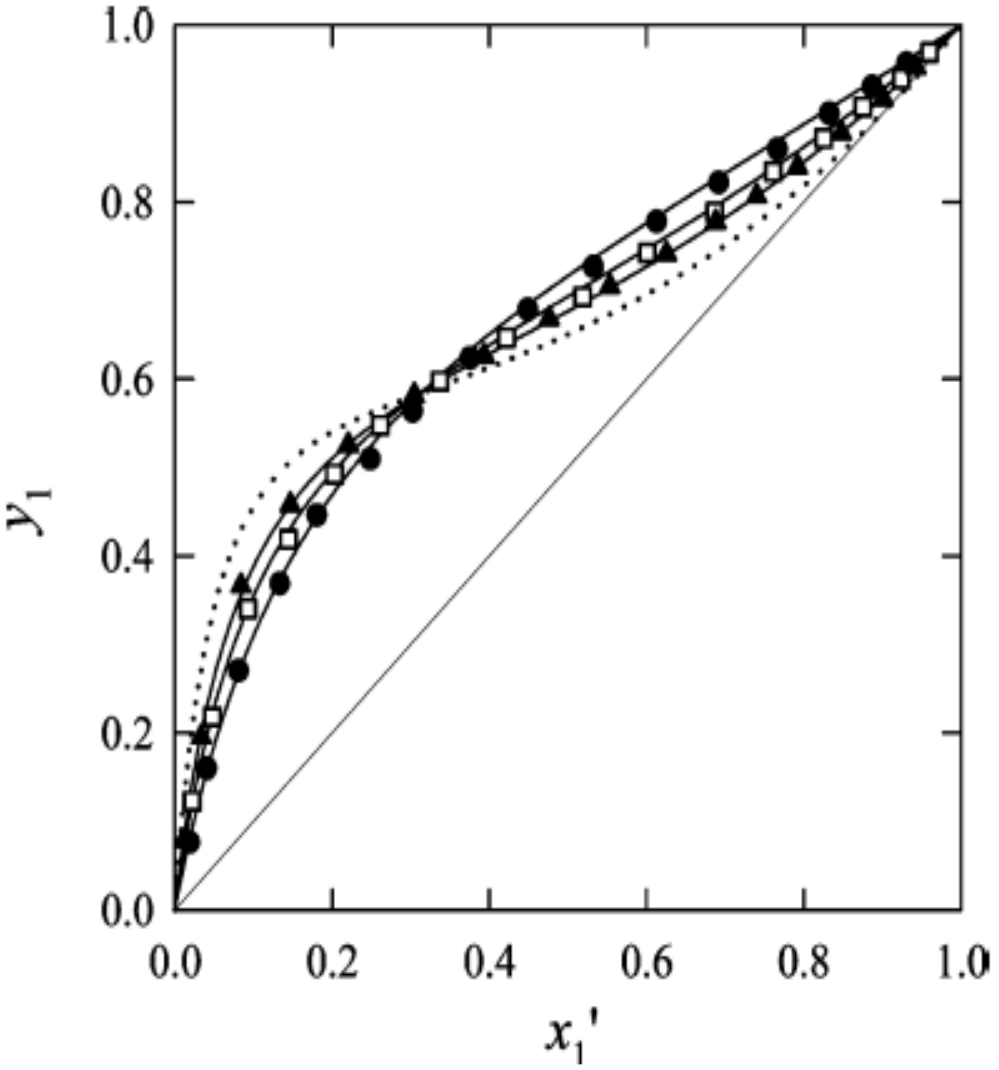
H.-J. Huang et al. / Separation and Purification Technology 62 (2008) 1–21

Introduction

▸ Extractive Distillation with Ionic Liquids



John Wiley, Biofuels, Bioprod. Bioref. 2:553–588 (2008)

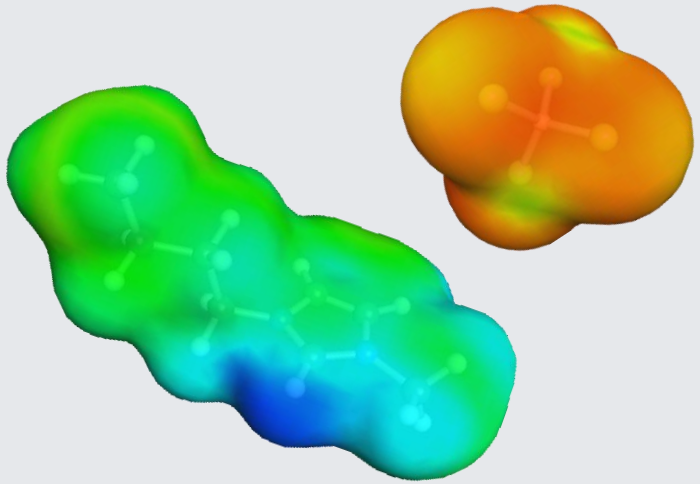


Journal of Chemical & Engineering Data, Vol. 55, No. 4, 2010

Introduction

▸ Ionic Liquids

- **Molten salts**, liquid at room temperature
- **Bulky and Asymetric** cation
- **Several** types of anion (halides, inorganic, organic)



- Low melting point (<100ºC)
- Non flammable
- Negligible vapor pressure
- Good thermal stability
- Possibility of tune their properties for specific task

Task - specific

Properties are related to the cation and anion that built the Ionic Liquid:

- Hydrophobicity
- Viscosity
- Density

Structure – Property relations

Introduction

▸ Ionic Liquids

Large number of potential ILs → Unfeasibily to Study experimentaly

↓

Normally used:
Group contribution method

Predictive models

⟷

Hildebrand solubility parameter

- Experimental Data
- Theory

Ionic Liquid as entrainer

Extractive Distillation

Hildebrand

$$\delta = \left(\frac{\Delta U}{V} \right)^{1/2}$$

The Hildebrand theory was developed for **Regular Solutions**:

- Systems with negligible excess volume and excess entropy

$$G^E = U^E$$

Hildebrand and Scatchard equation for free Gibbs energy

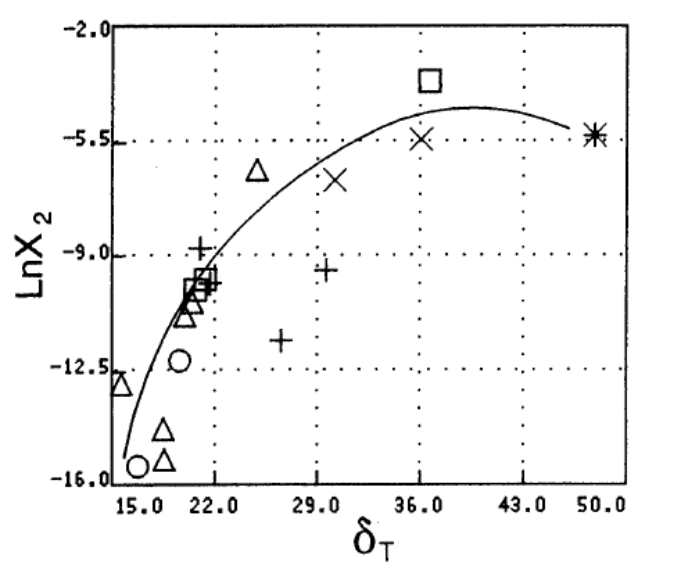
Relation with solubility parameter

$$G^E = U^E = \Phi_1 \Phi_2 (\delta_1 - \delta_2)^2 (x_1 V_1 + x_2 V_2)$$

To estimate the **solubility parameter** they suggested that experimental data according to:

$$\delta_i = \sqrt{\frac{\Delta U^{vap}}{V_i}} = \sqrt{\frac{\Delta H^{vap} - RT}{V_i}}$$

Or: using the **mole fraction solubility**

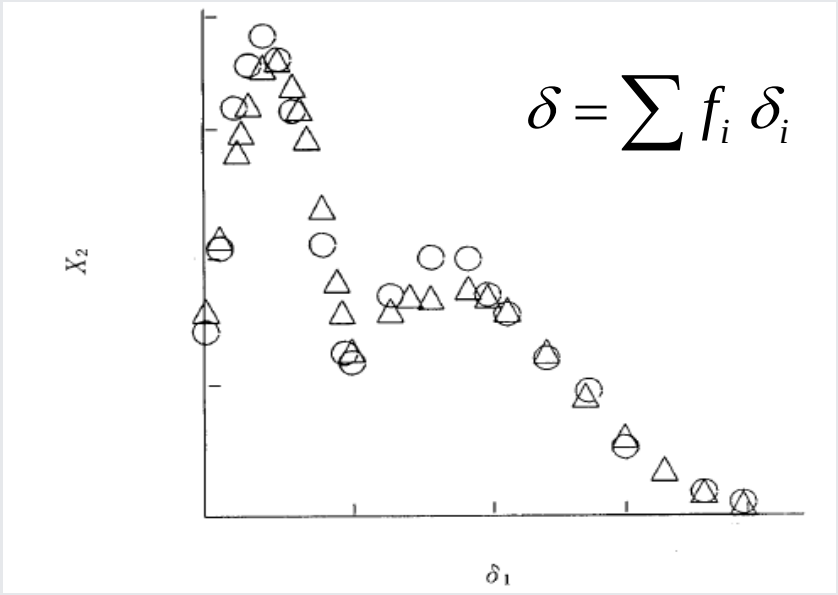


Maximum of solubility corresponds to the value of the overall solubility parameter for the compound in study.

Peña M, Bustamante P, Chem Pharm. Bull. 48(2) 179-183 (2000)

Introduction

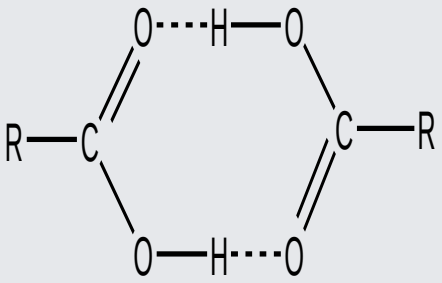
▸ Solubility Parameter



❖*Chamaleonic effect*

Defined by Hoy:

- **Two** different behaviours accordingly to the solvents present in the medium



Bustamante.P, Chem & Pharm Bull, 1994. ***42****(5): p. 1129-1133*

Introduction

Solubility Parameter

- How does solubility parameter helps on the process of Extractive distillation?

$$RT \ln(\gamma_j) = V_j \Phi_i^2 (\delta_i - \delta_j)^2$$

Regular Solution Theory

$$S_{ij} = \frac{\gamma_i}{\gamma_j}$$

Selectivity

Selectivity is an indicator of a promising solvent for one specific mixture

Establishment of a solubility parameters scale

Choise of the best IL

Estimation of solubility parameters:

- Density
- **Viscosity**
- Surface tensions
- Lattice energy
- Melting points
- **Activity Coefficients at infinite dilution**

Estimation of Solubility Parameters

Activity Coefficients at infinite dilution

One of the most important thermodynamic properties is the activity coefficient which is related to the excess free Gibbs energy by,

$$G^E = RT \sum_i x_i \ln(\gamma_i)$$

Combining:

- previous equation with the one obtained by Hildebrand for G^E with solubility parameter

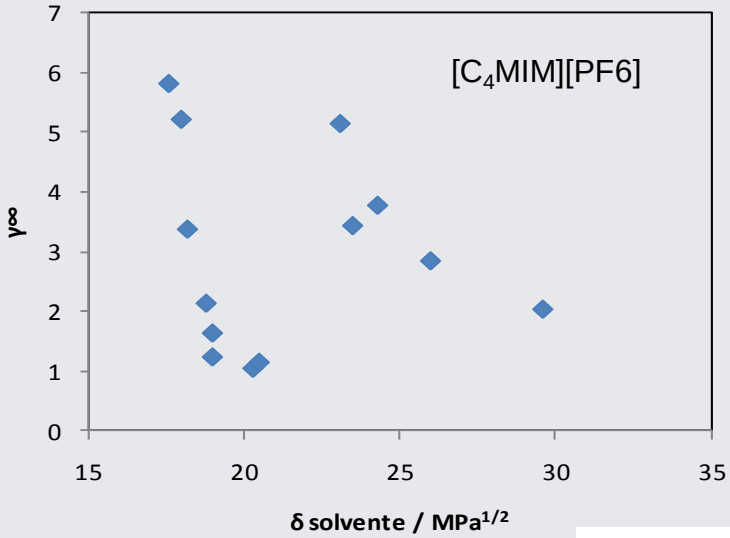
-Applying infinite dilution conditions, $\Phi_i=1$ and $\gamma_i = \gamma^\infty$

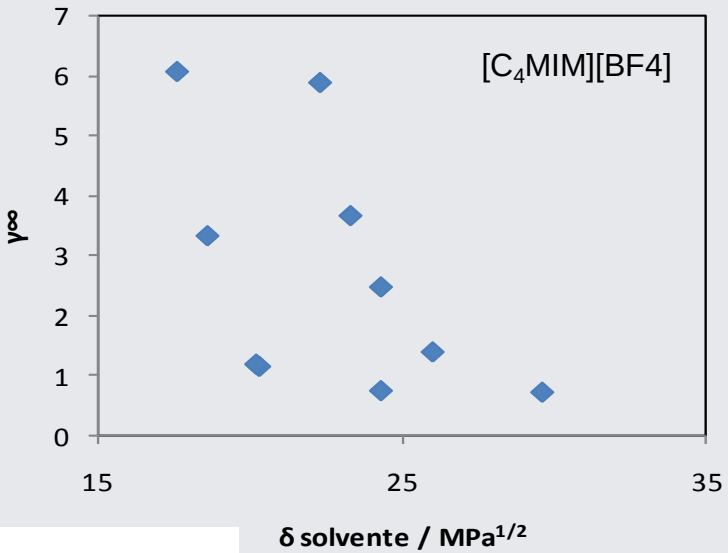
$$RT \ln\left(\gamma^\infty\right) = V_j \left(\delta_i - \delta_j\right)^2 \quad \rightarrow \quad \delta_i = \delta_j + \left(\ln\left(\gamma^\infty\right) \frac{RT}{V_j} \right)^{1/2}$$

Estimation of Solubility Parameters

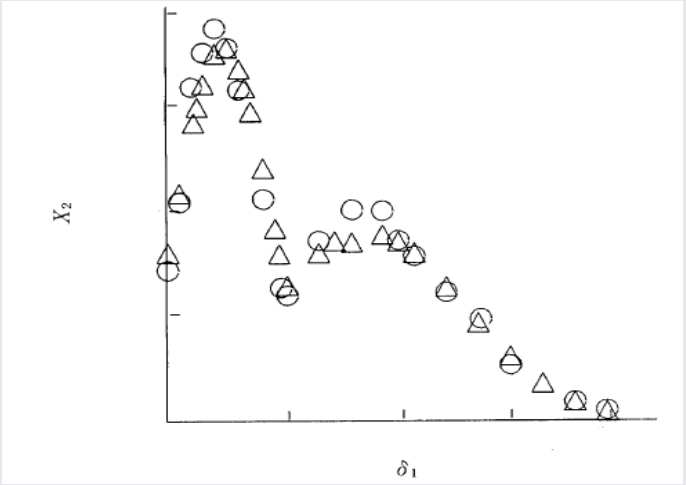
▸ Activity Coefficients at infinite dilution - Results & Discussion

Collected data





$$\gamma = \frac{1}{x}$$



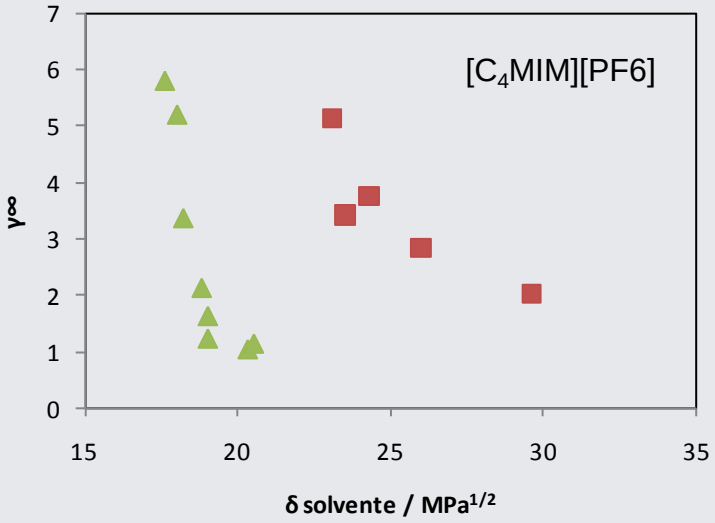
Chameleonic Effect

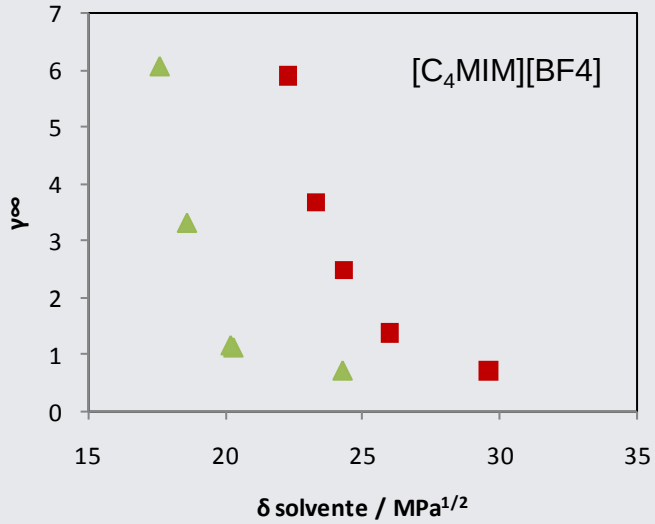
Estimation of Solubility Parameters

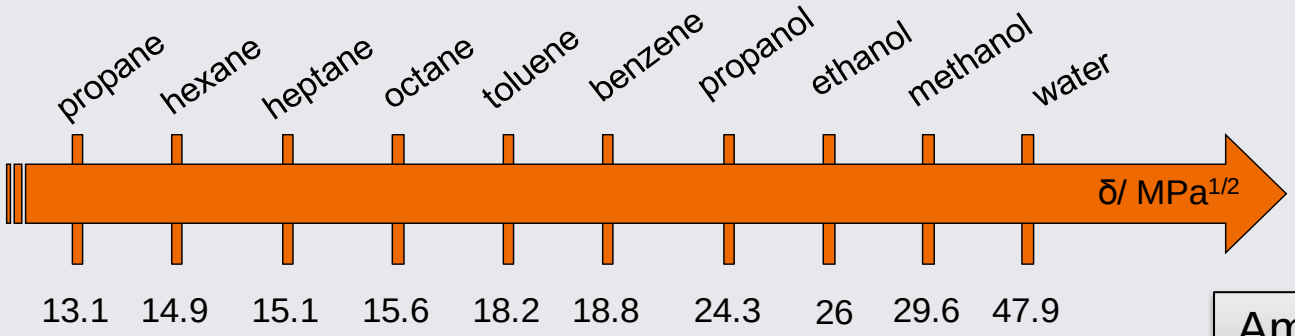
▸ Activity Coefficients at infinite dilution - Results & Discussion

http://path.web.ua.pt

Collected data







Amphiphilic Characteristic of ILs

Estimation of Solubility Parameters

Activity Coefficients at infinite dilution - Results & Discussion

- Estimation for **two solubility parameters:**

δ_{NP} – NONPOLAR families;

δ_{P} – POLAR families

Temperature 298.15K

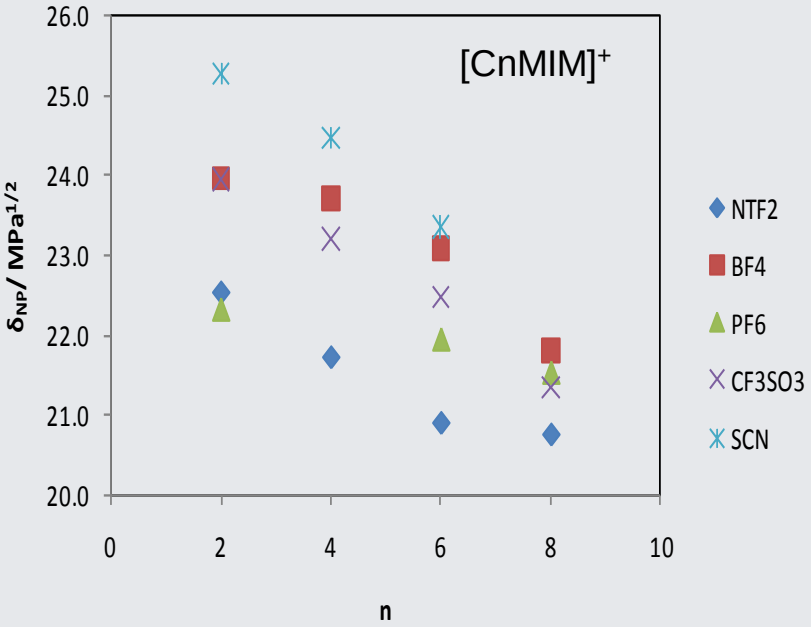
Data for δ_j and V_j were collected from literature at 298.15 K

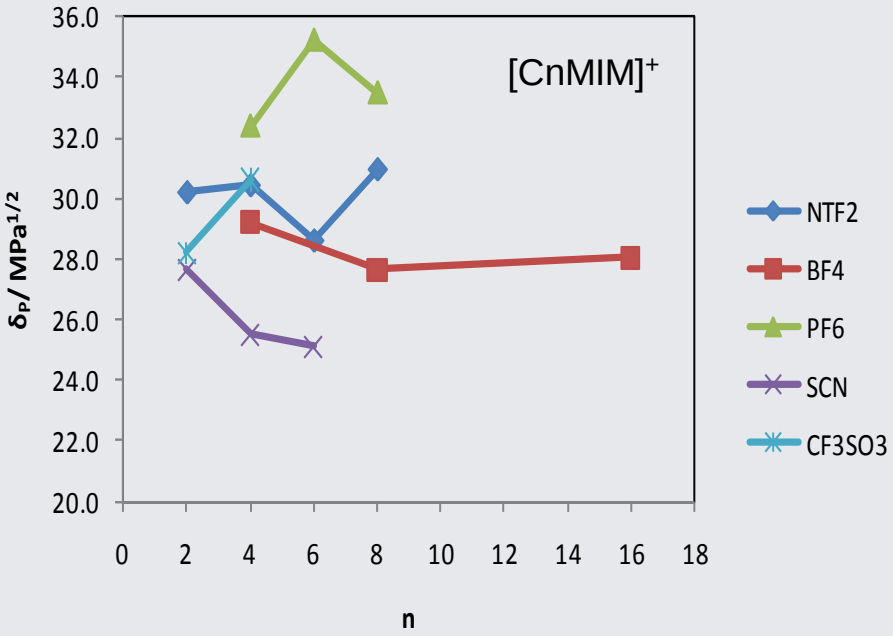
Data for γ^{∞} were collected from available data published at different temperatures

Estimation of Solubility Parameters

▸ Activity Coefficients at infinite dilution - Results & Discussion

Alkyl chain length effect

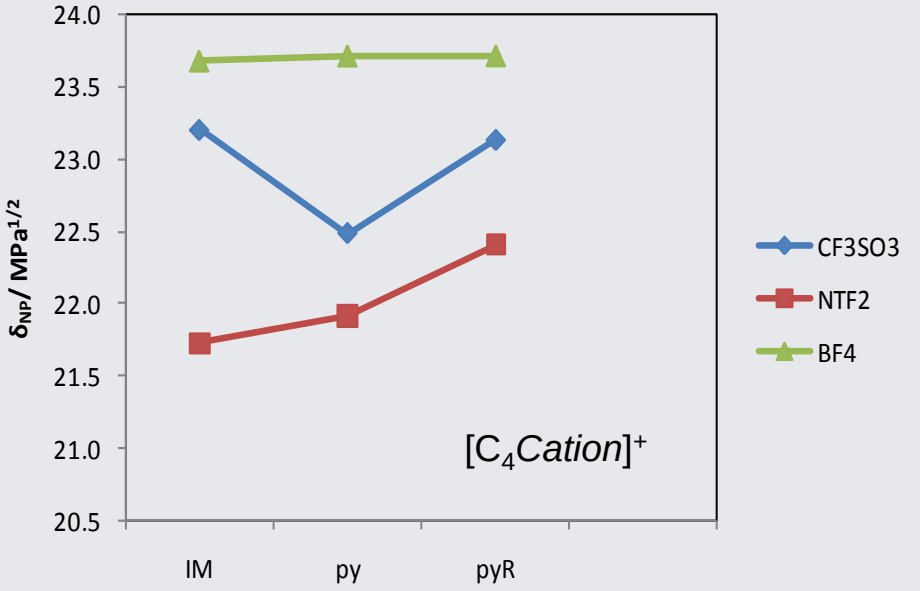


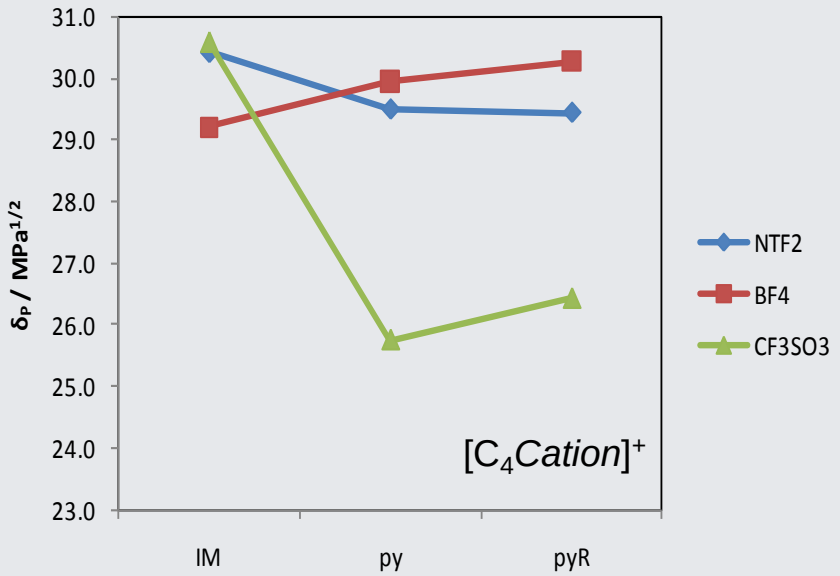


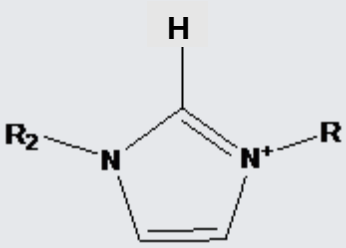
Estimation of Solubility Parameters

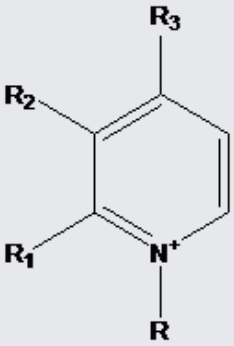
▸ Activity Coefficients at infinite dilution - Results & Discussion

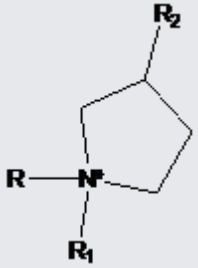
Cation family effect









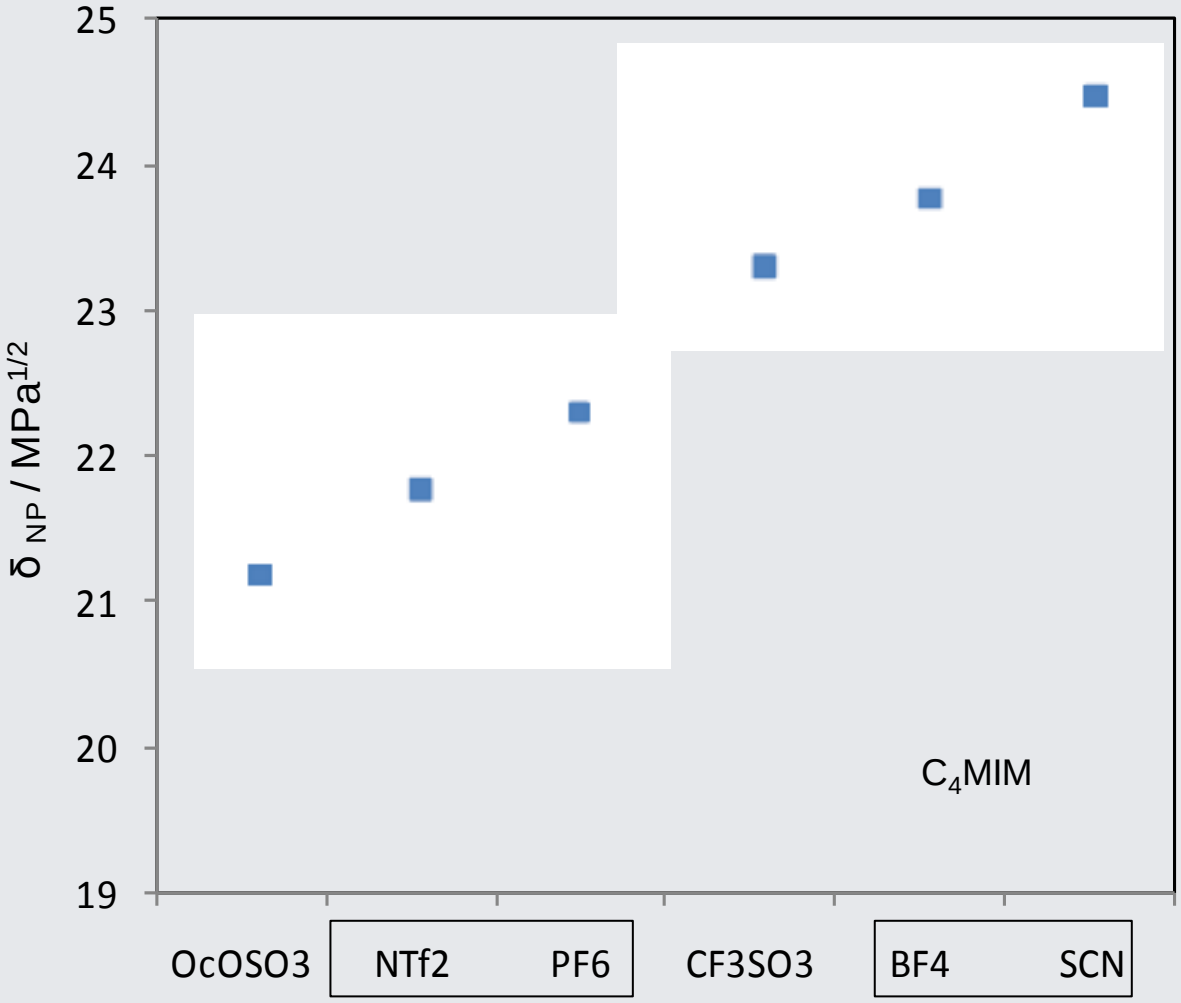


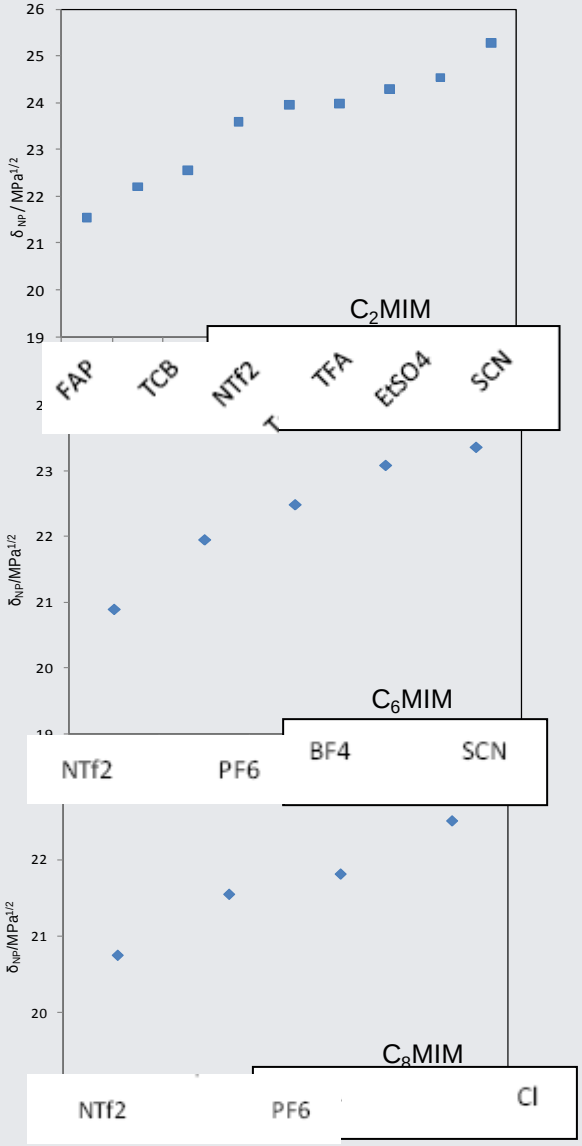
Estimation of Solubility Parameters

▸ Activity Coefficients at infinite dilution - Results & Discussion

http://path.web.ua.pt

Anion effect



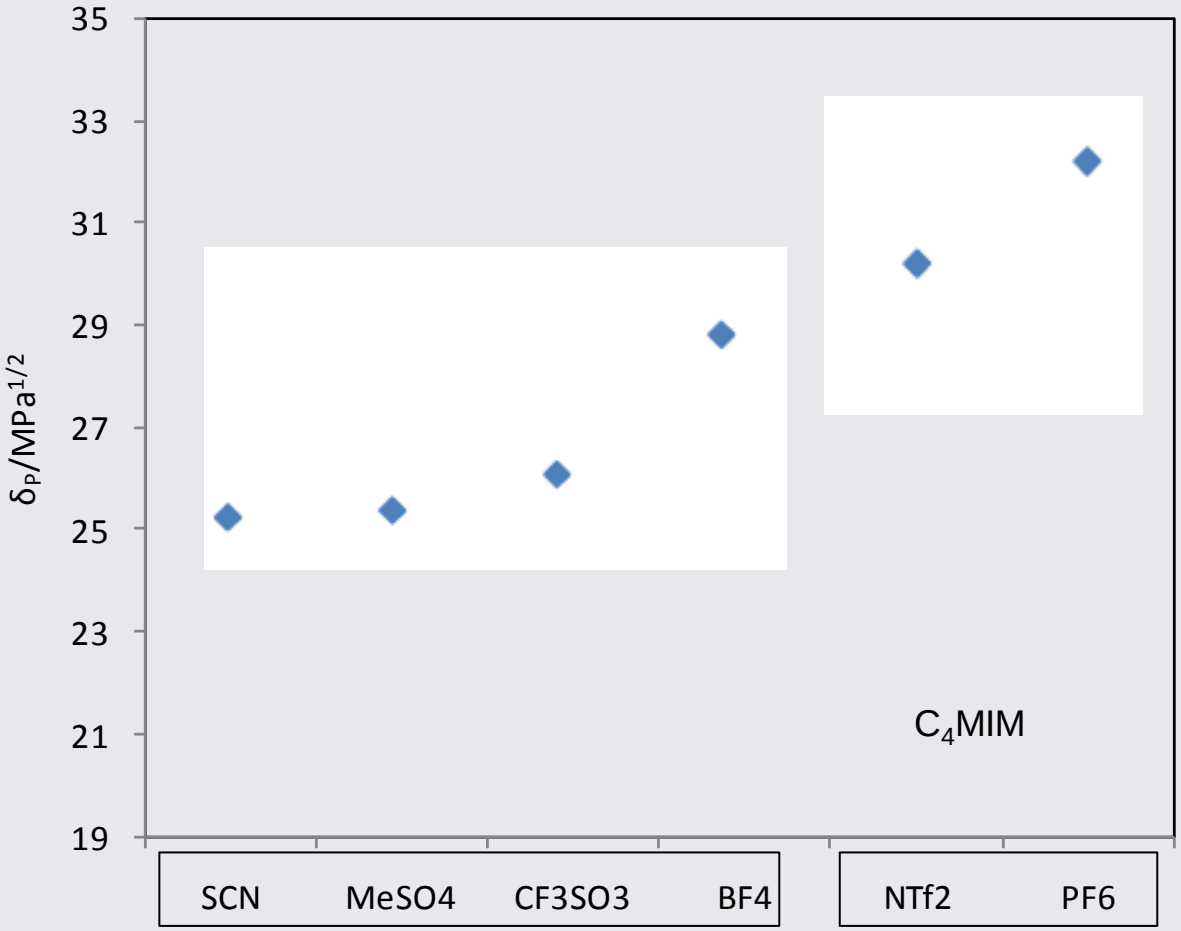


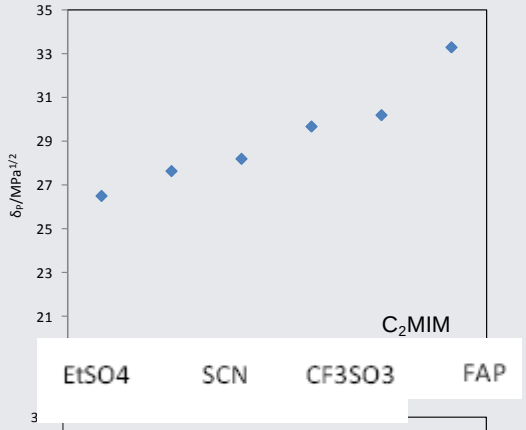
Estimation of Solubility Parameters

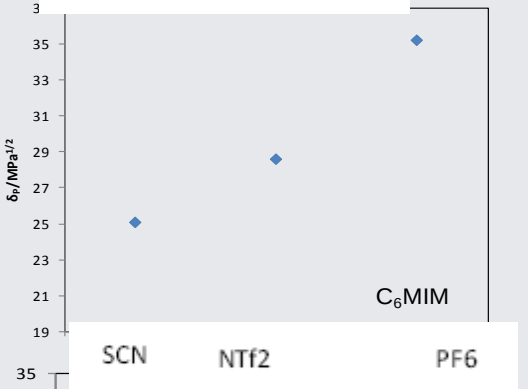
▸ Activity Coefficients at infinite dilution - Results & Discussion

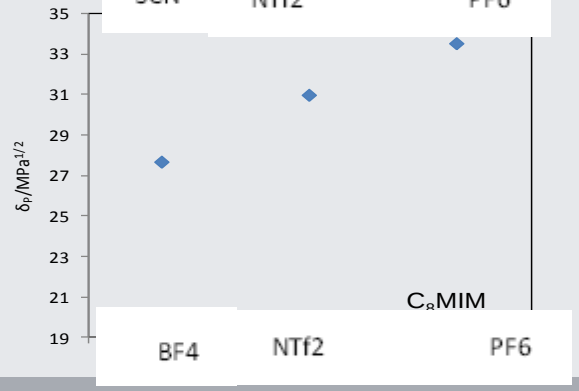
http://path.web.ua.pt

Anion effect





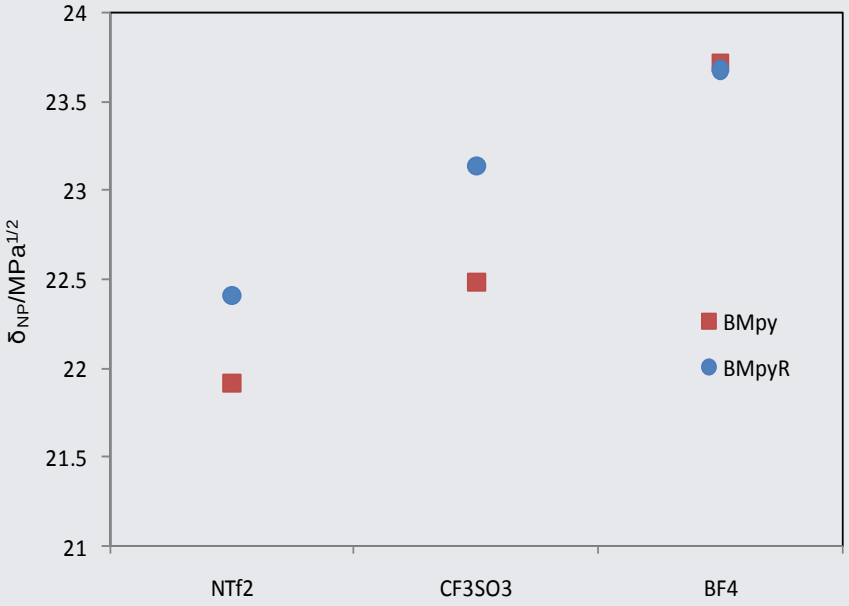


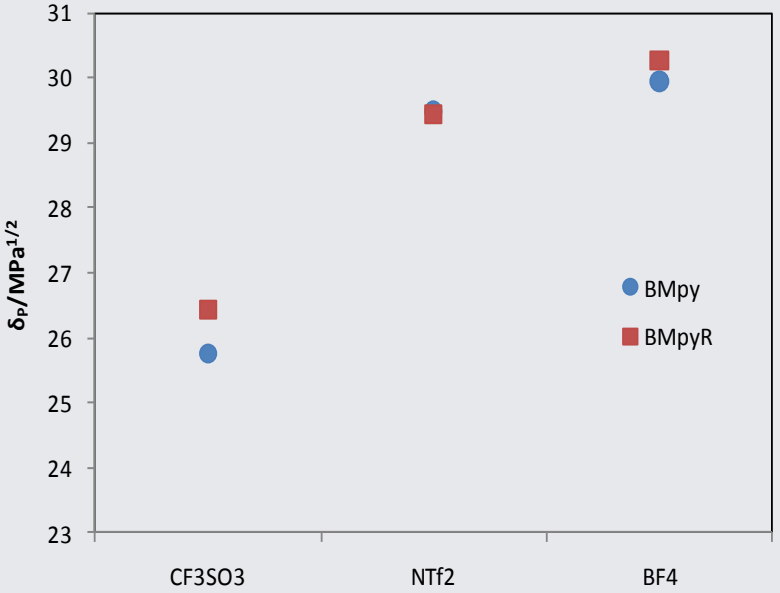


Estimation of Solubility Parameters

▸ Activity Coefficients at infinite dilution - Results & Discussion

Anion effect





Estimation of Solubility Parameters

Viscosity

*Kilaru, P.K. and P. Scovazzo, Industrial & Engineering Chemistry Research, 2008. **47**(3): p. 910-919.*

$$\Delta G_{vis}^{0} = RT \ln\left(\frac{\mu V_1}{hN_A}\right)$$

viscosity
with
molar energy of activation

$$E^{vap} = K_v \Delta G_{vis}^{0}$$

energy of vaporization
with
molar free energy of activation

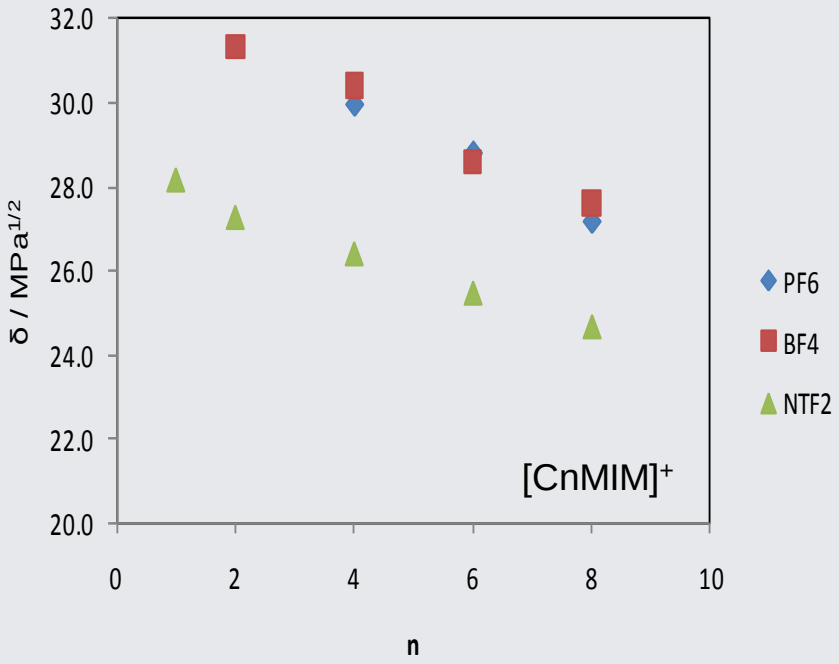
$$\delta_1 = \left\{\frac{K_v RT}{V_1} \ln\left[\frac{\left(1\times10^{-9}\right)\mu V_1}{hN_A}\right]\right\}^{1/2}$$

Solubility parameter for pure Ionic Liquid

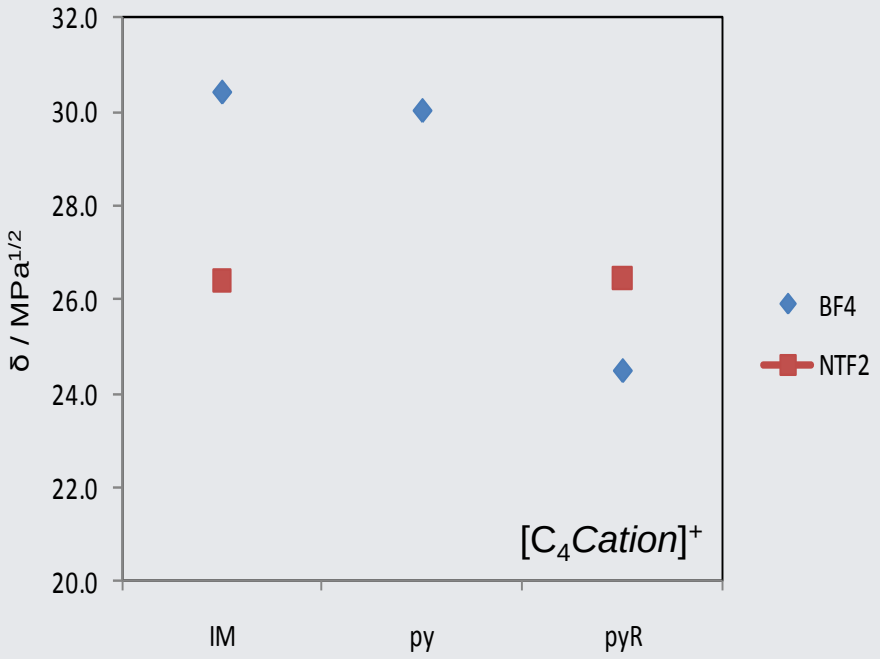
Estimation of Solubility Parameters

▸ Viscosity - Results & Discussion

Alkyl chain length effect



Cation family effect

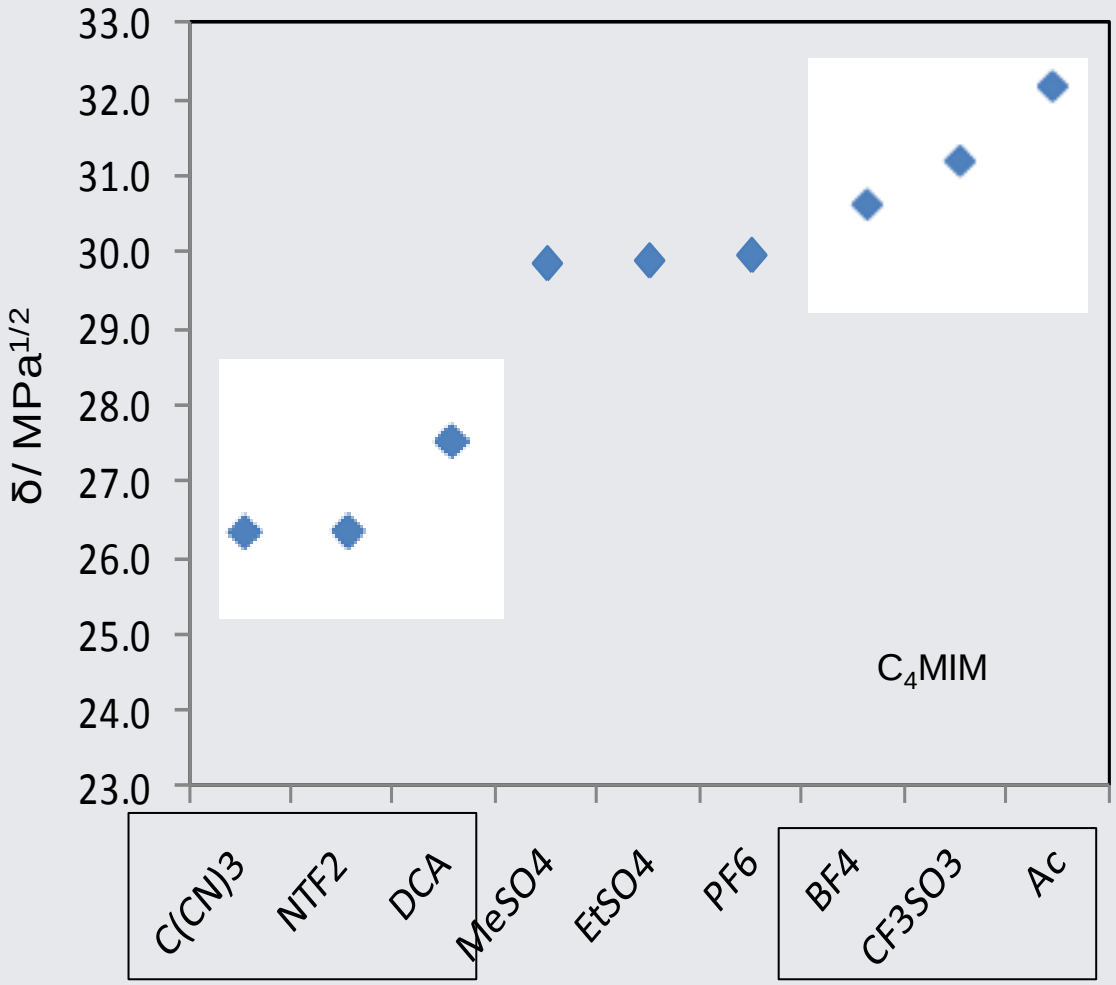


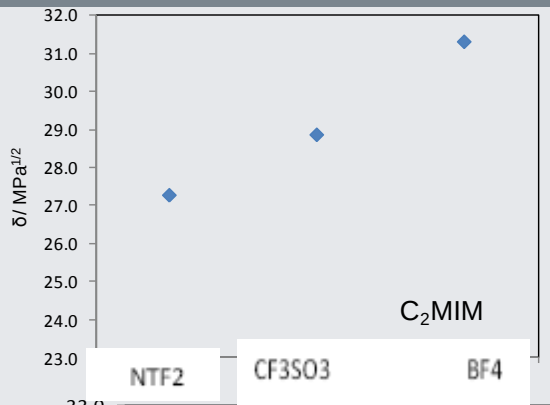
Estimation of Solubility Parameters

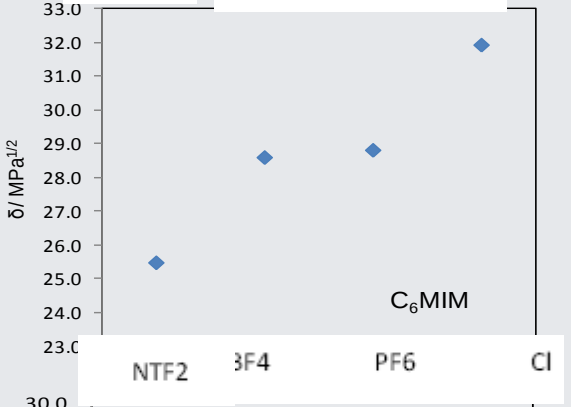
▸ Viscosity - Results & Discussion

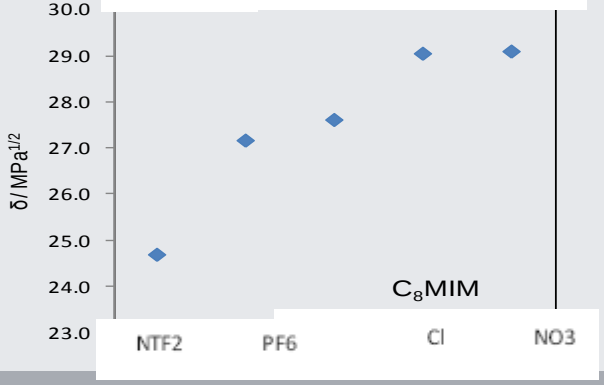
http://path.web.ua.pt

Anion effect



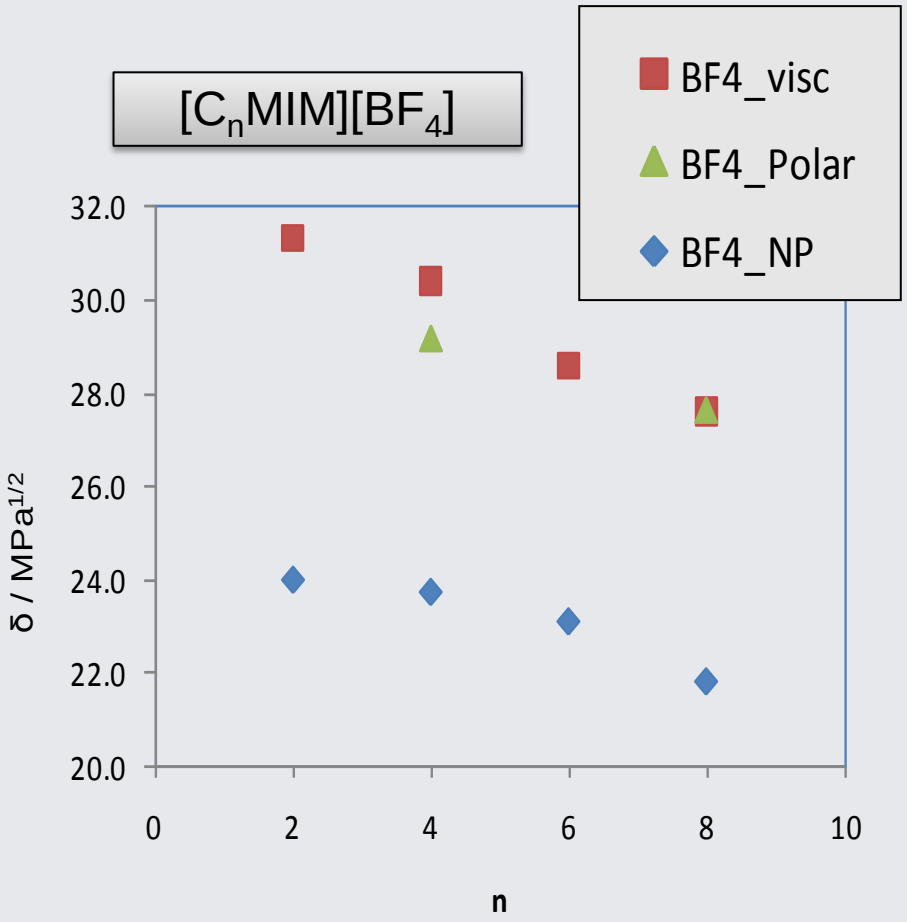


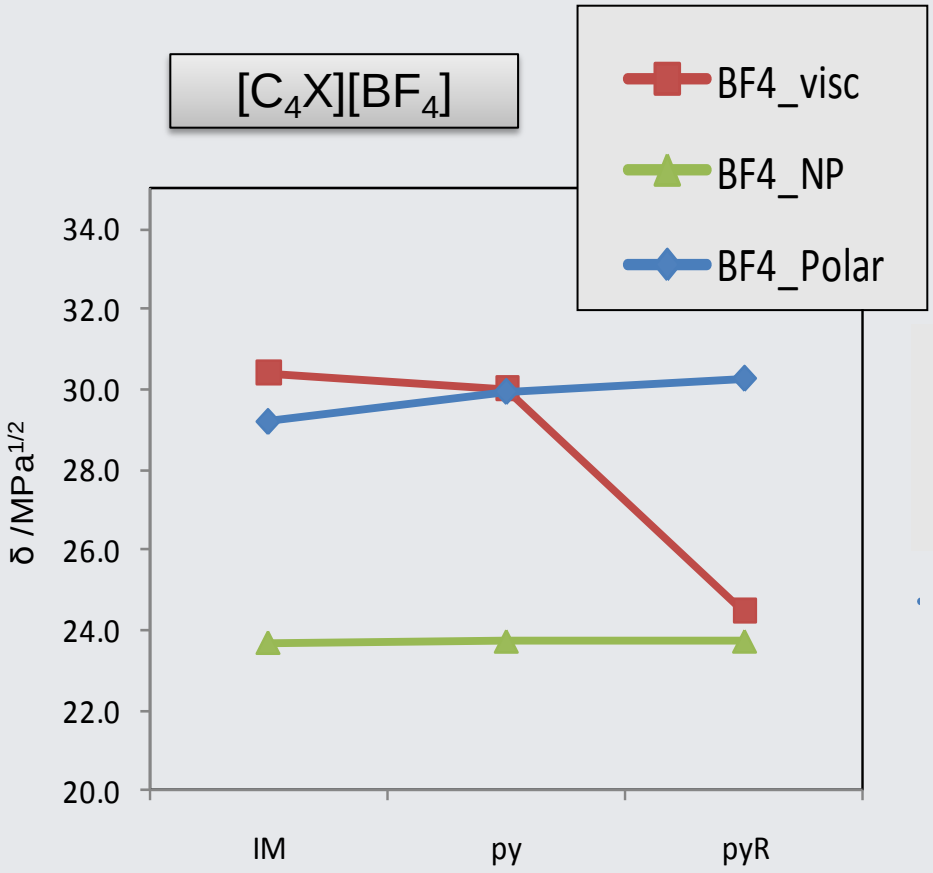




Estimation of Solubility Parameters

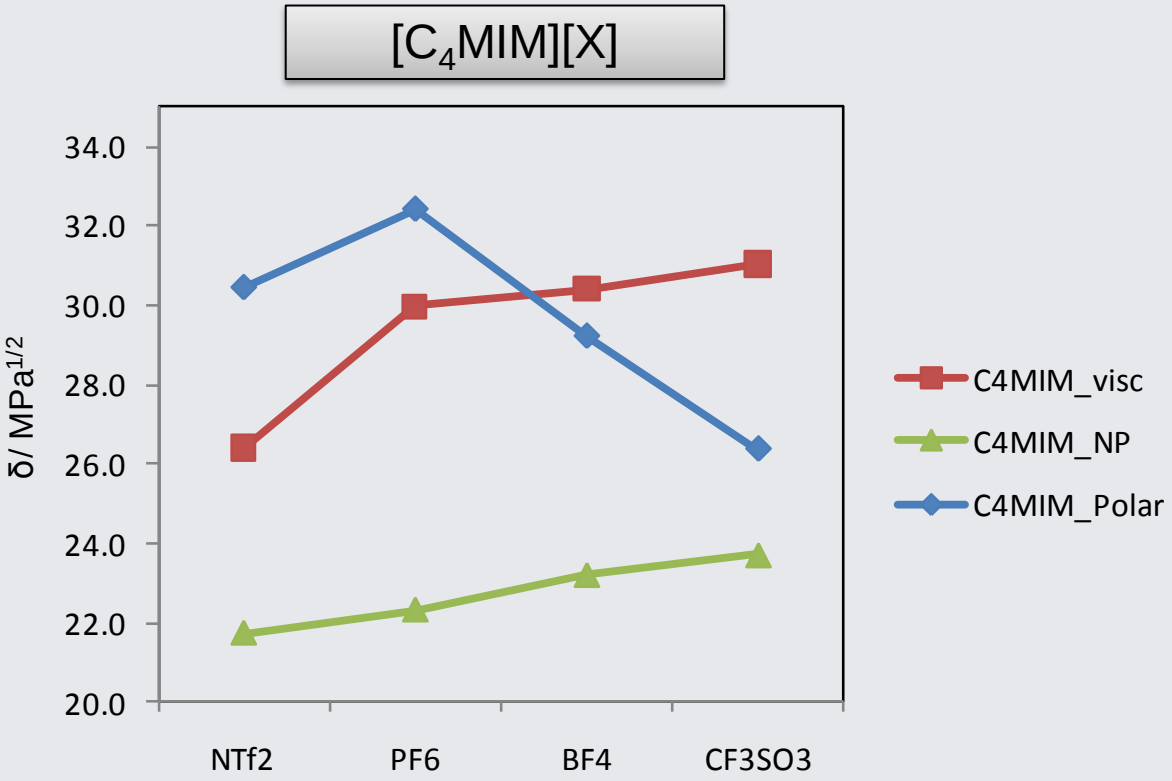
- Viscosity vs Activity coefficient at infinite dilution





2 Estimation of Solubility Parameters

▸ Viscosity vs Activity coefficient



- The values obtained for viscosity are closer to the solubility parameters for polar family
- The behavior is similar to solubility parameters for nonpolar family

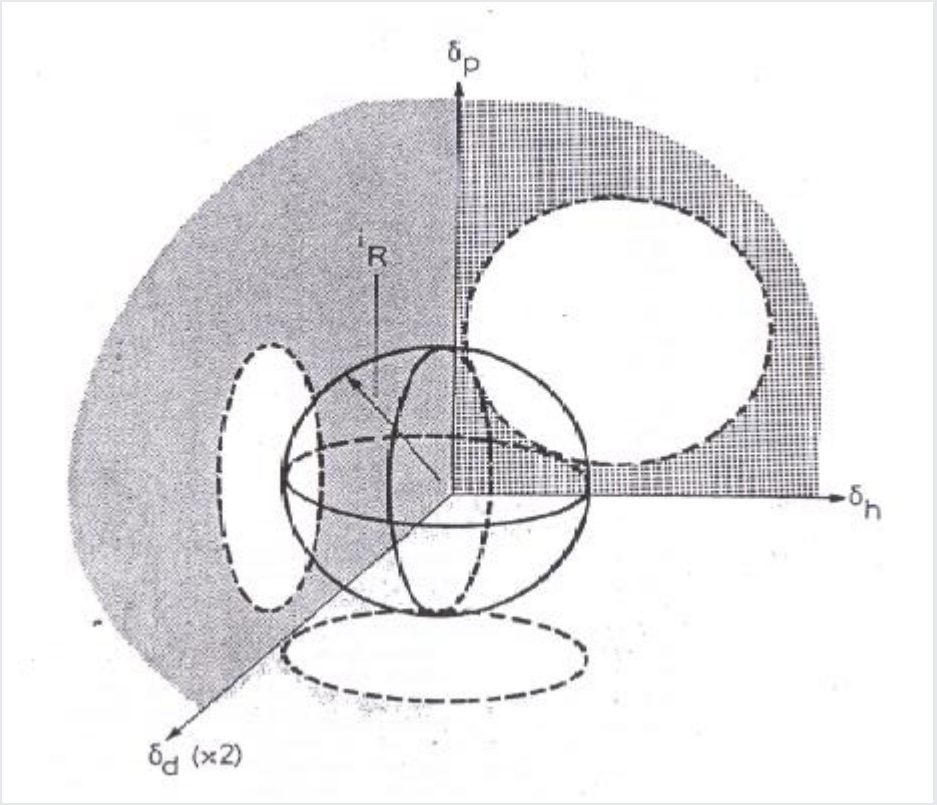
Estimation of Solubility Parameters

The regular solution theory, proposed by Hildebrand has proved to be useful to predict phase behaviour of solutions without detailing molecular polarity or specific interactions

Hansen

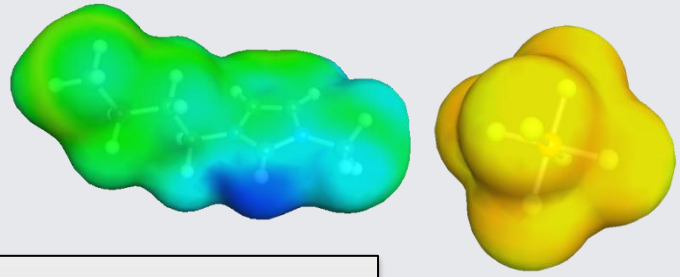
$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

Each interaction is accounted

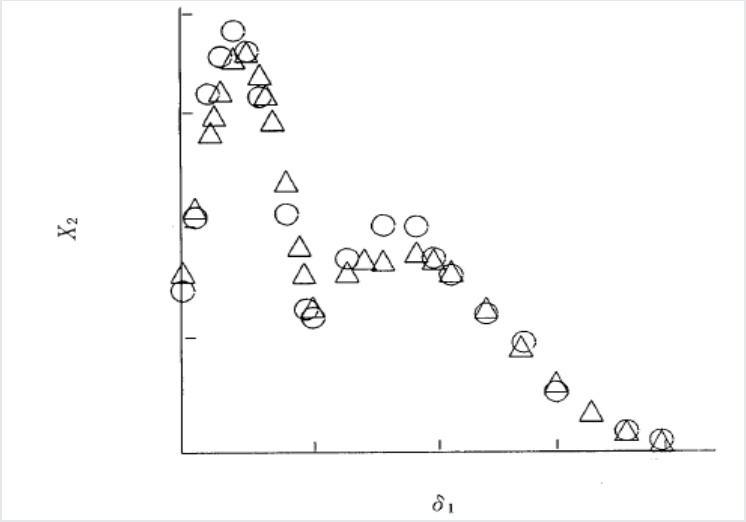


Experimental Section

Ionic Liquid in study:
$[C_4MIM][PF_6]$



Determination of the solubility of this IL at mixtures with different compositions namely,15, 30, 45, 60, 75 and 90% of 1-propanol and water, 1-propanol and toluene.



Experimental Section

IL in water and 1-propanol

UV

Experimental Section

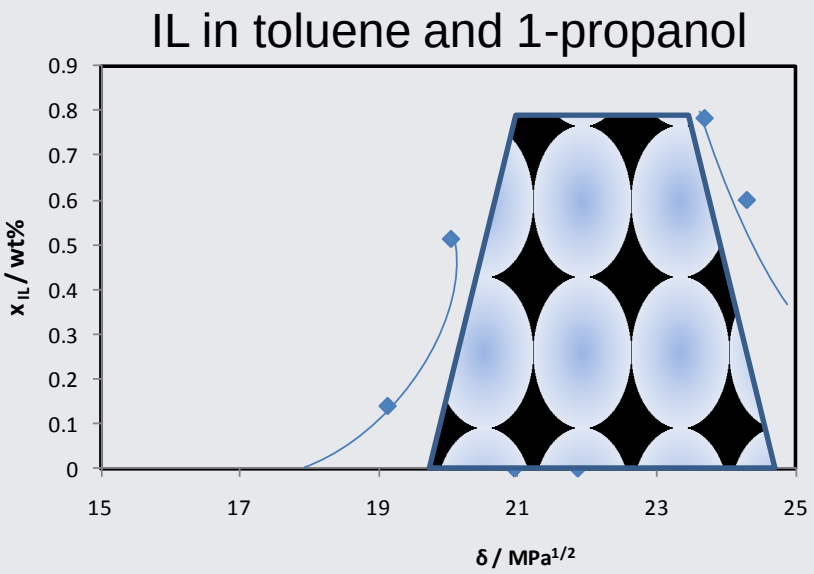
IL in toluene and 1-propanol

Gravimetric Method

Experimental Section

Results and discussion

$$\delta = \sum f_i \, \delta_i$$



1-propanol / vv%	δ / MPa$^{1/2}$	x $_{IL}$ / wt%
85	19.115	0.140
70	20.03	0.513
55	20.945	Miscible
40	21.86	Miscible
25	22.775	0.149
10	23.69	0.782
0	18.2	0.098

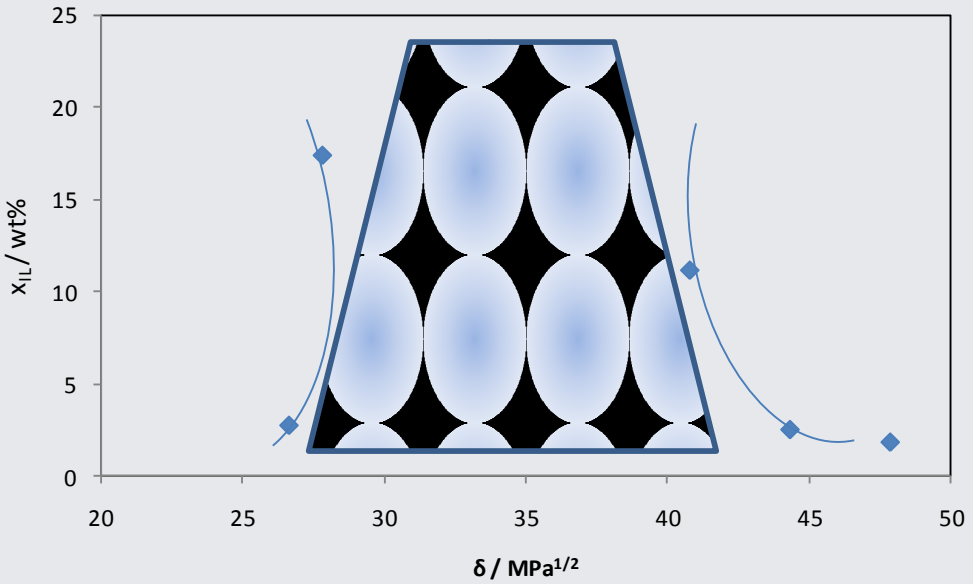
δ_{NP}= 22.34 MPa$^{1/2}$, δ=29.98 MPa$^{1/2}$

Experimental Section

Results and discussion

$$\delta = \sum f_i \, \delta_i$$

IL in water and 1-propanol



1-propanol / vv%	δ / MPa$^{1/2}$	x $_{IL}$ / wt%
0	47.9	1.875
15	44.36	2.556
30	40.82	11.202
45	37.28	12.030
60	33.74	23.204
85	27.84	17.435
90	26.66	2.787
100	24.3	0.600

δ_P=32.4 MPa$^{1/2}$, δ=29.98 MPa$^{1/2}$

Conclusions

- An **amphiphilic (Chamaleonic) behavior** of the ILs is observed when solubility parameters are estimated from activity coefficients at infinite dilution;

- The use of viscosity to estimate the solubility parameter shows that pure ILs **act predominantly as a polar molecules**. Values for solubility parameters equivalent to those obtained in presence of polar solvents are obtained;

- Solubility measurements **confirm the behavior** observed with infinite dilution activity coefficients;

- It is shown that the Hildebrand solubility parameters (unidimensional) cannot adequately describe the ILs behavior; The use of the Hansen's approach is suggested.

Future Work

Given the complexity of interactions, for future work it would be interesting to work in the solubility parameters through Hansen's theory which takes accounts three different contributions,

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

Acknowlegdements

- Professor João A.P Coutinho
- Path group