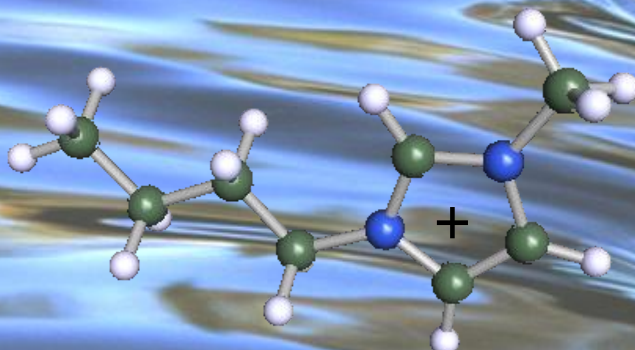
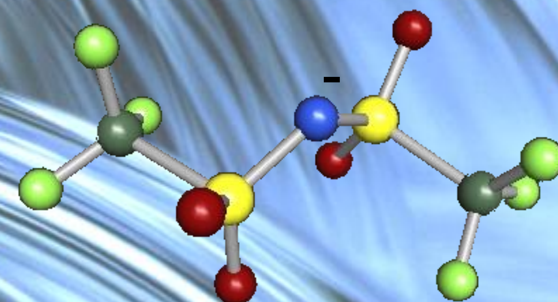
universidade de aveiro

PATh

Treatment of Aqueous Effluents Contaminated with Ionic Liquids





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Summary

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1. Introduction

1.1 ILs – ILs properties

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Ionic Liquids (ILs)

Cations ✚ Anions

-Large
-Organic
- Asymmetric

-Organic or inorganic

Do not have a crystalline form!

Liquids at $T \leq 373$ K and $p = 1$ atm

1. Introduction

1.1 ILs – ILs properties

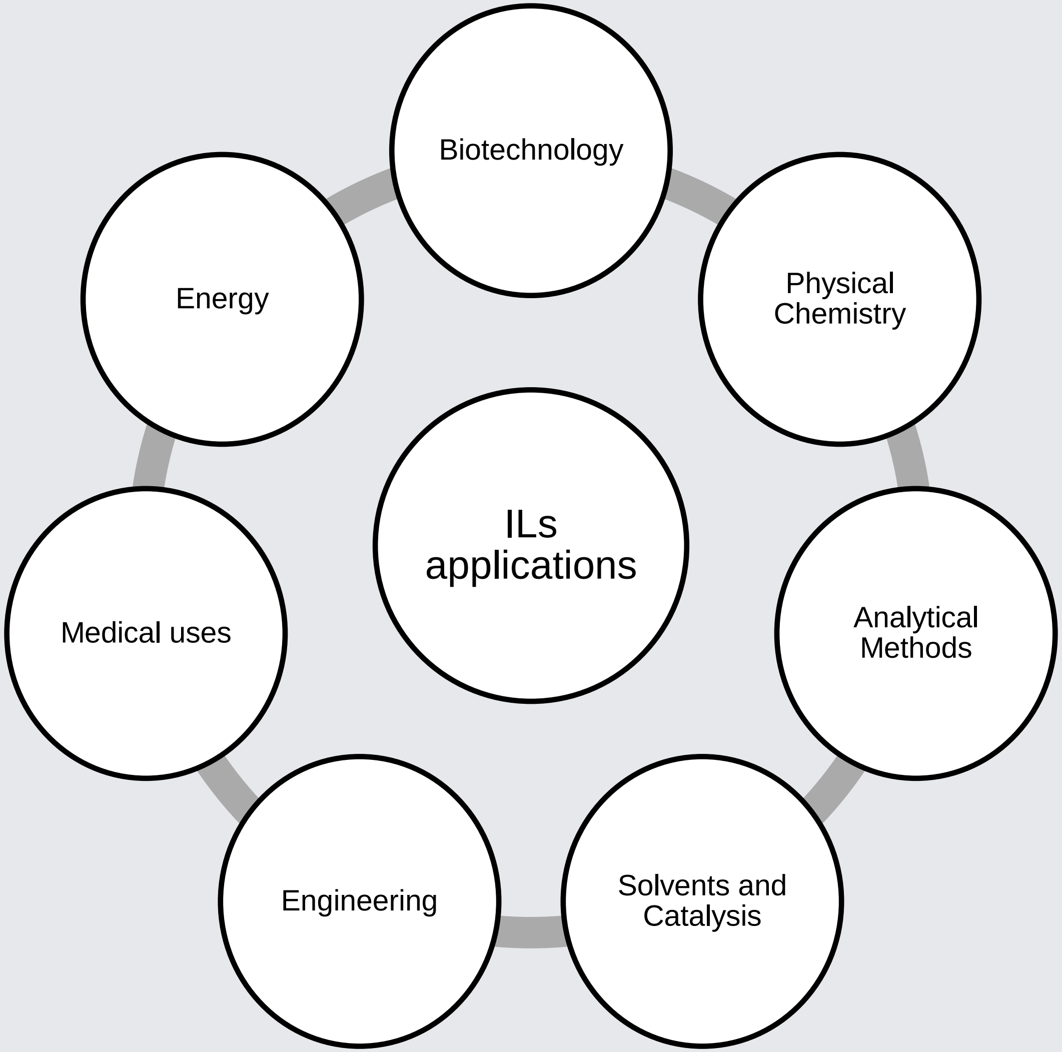
Property	ILs
Chemical stability	High
Thermal stability	High
Nº of Combinations	$> 10^6$
Melting Temperature	Low
Vapour Pressure	Low

"Designer solvents"

"Green solvents"

1. Introduction

1.2 ILs – ILs applications



Toxicity tests with luminescent marine bacteria *Vibrio fisheri** (15 min)

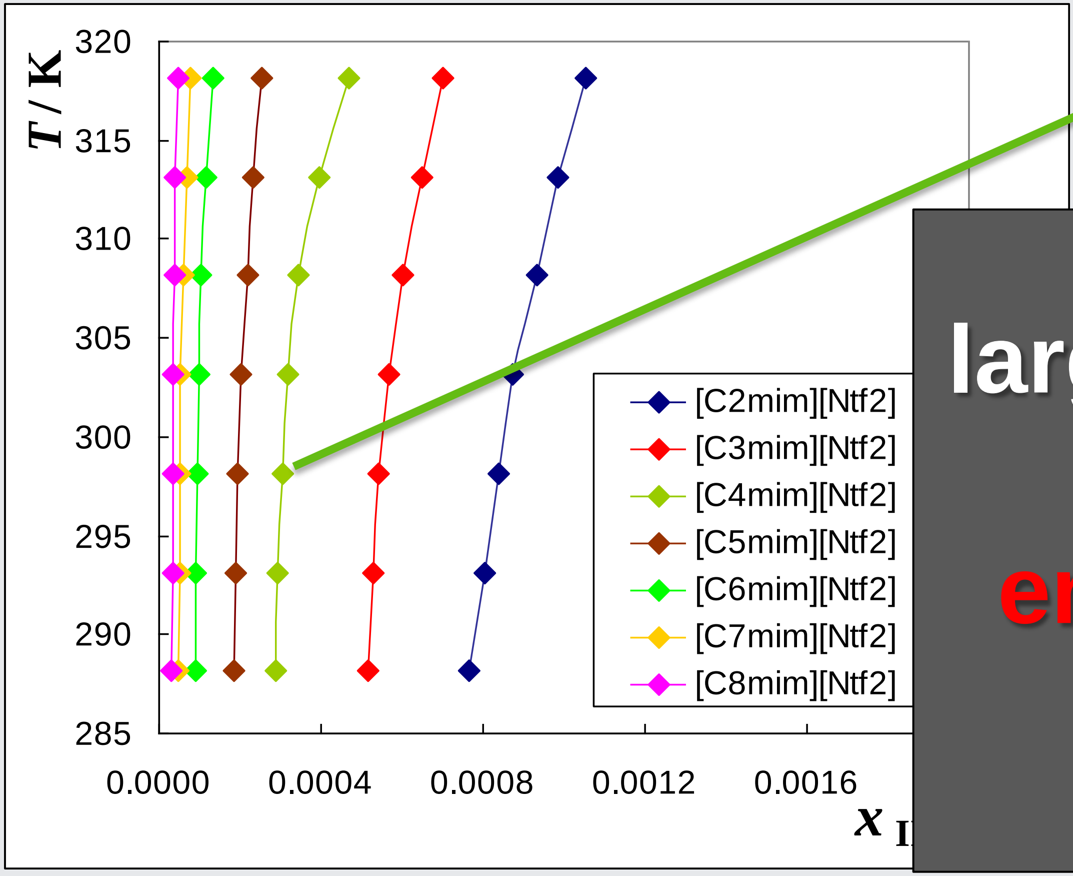
ILs	$Log(EC_{50}$ / µM)	VOCs	$Log(EC_{50}$ / µM)
$[C_4mim][BF_4]$	3.55	Methanol	5.00
$[C_5mim][BF_4]$	3.14	Acetone	4.29
$[C_6mim][BF_4]$	2.15	Dichloromethane	3.40
$[C_7mim][BF_4]$	2.44	Benzene	2.03
$[C_8mim][BF_4]$	1.41	Toluene	1.50
$[C_9mim][BF_4]$	0.72	Phenol	1.49
$[C_{10}mim][BF_4]$	-0.18	O-Xylene	0.97
$[C_4mim]Cl$	2.95		
$[C_4mim]Br$	3.07		
$[C_4py]Br$	2.73		
$[C_4mpy]Br$	2.12		
$[C_6mpy]Br$	1.48		
$[C_8mpy]Br$	0.25		

Lower $log(EC_{50})$

Higher Toxicity

*J. Kärkkäinen, Master Thesis, Department of Chemestry, University of Oulu, Finland, 2007.

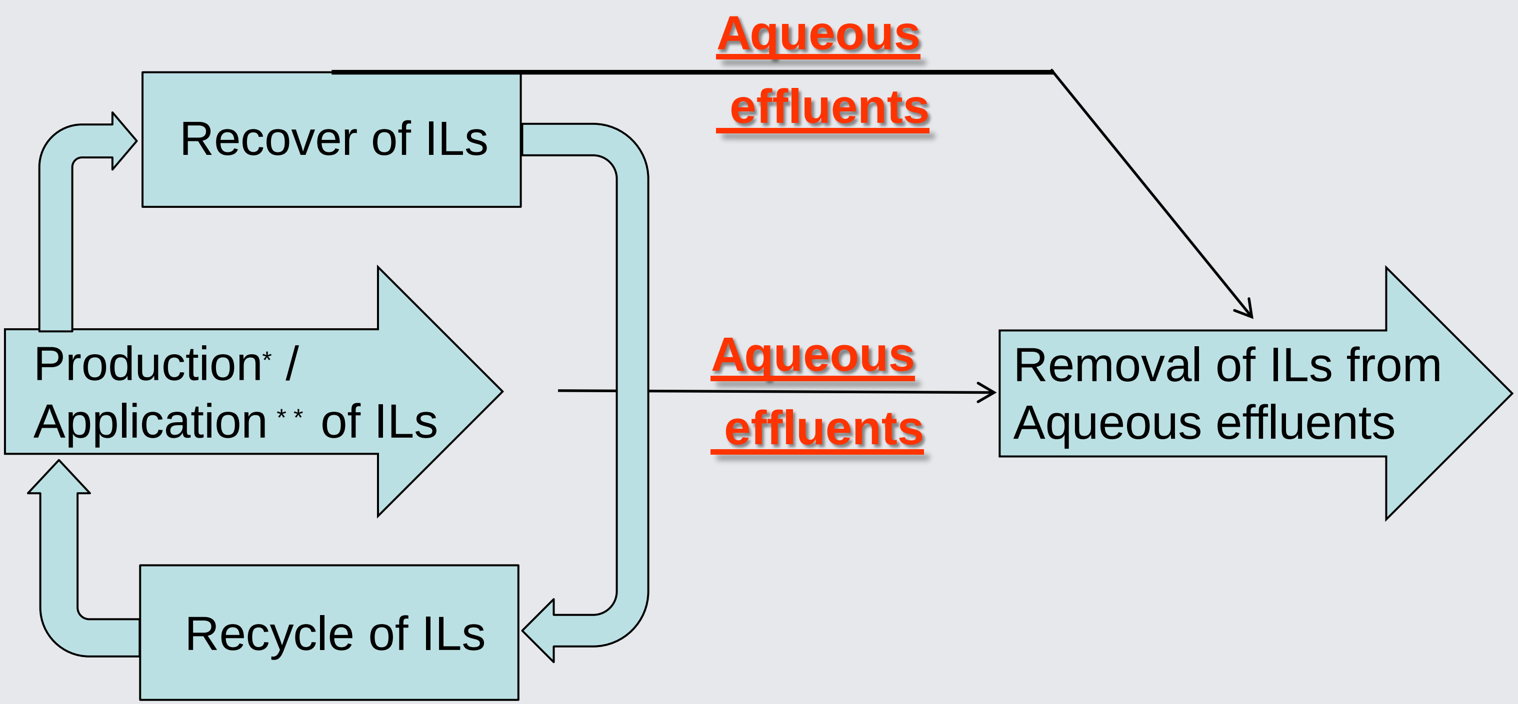
Non-negligible solubility in water* (even those considered hydrophobic)



≈ 0.72 wt %

Use in a **large scale** leads to **aquatic environmental impact**

*M. G. Freire, C. M. S. S. Neves, P. J. Carvalho, R. L. Gardas, A. M. Fernandes, I. M. Marrucho, L. M. N. B. F. Santos, and J. A. P. Coutinho, T*he Journal of Physical Chemistry B, vol. 111, pp. 13082-13089, 2007.*



How to Remove ILs?

*P. T. Anastas, P. Wasserscheid, and A. Stark, *Handbook of Green Chemistry, Volume 6: Ionic Liquids*, 2010
**A. Kokorin, *Ionic Liquids: Theory, Properties, New Approaches*. InTech, 2011

2. Methods to remove ILs

2.1 Water treatment methods

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- **Oxidative Methods***
  - ILs degradation
  - By products
- **Thermal Methods****
  - ILs degradation
  - Very high temperatures
  - By products
- **Biological Methods*****
  - ILs degradation
  - Low biodegradability

*T. P. Thuy Pham et al., *Water Research,* vol. 44, pp. 352-372, 2010
**A. Kokorin, *Ionic Liquids: Theory, Properties, New Approaches*. InTech, 2011
***C. Abrusci, et al., *Green Chemistry,* vol. 13, pp. 709-717, 2011

2. Methods to remove ILs

2.1 Proposed methods to water treatment

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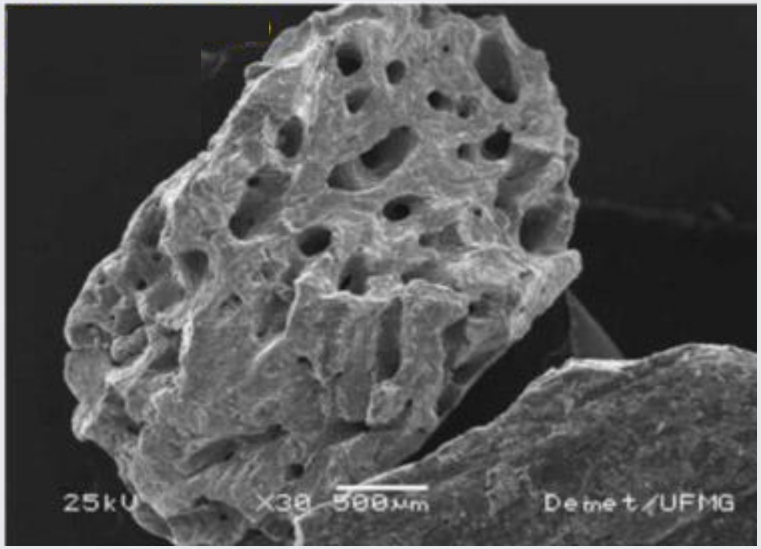
Adsorption for **Hydrophobic**
ILs onto Activated Charcoal

- ❑ **Highly developed porosity**
- ❑ **High surface area**



- ❑ **Special surface reactivity**
- ❑ **Highly inert**

- ❑ **Thermally stable**

2. Methods to remove ILs

2.1 Proposed methods to water treatment

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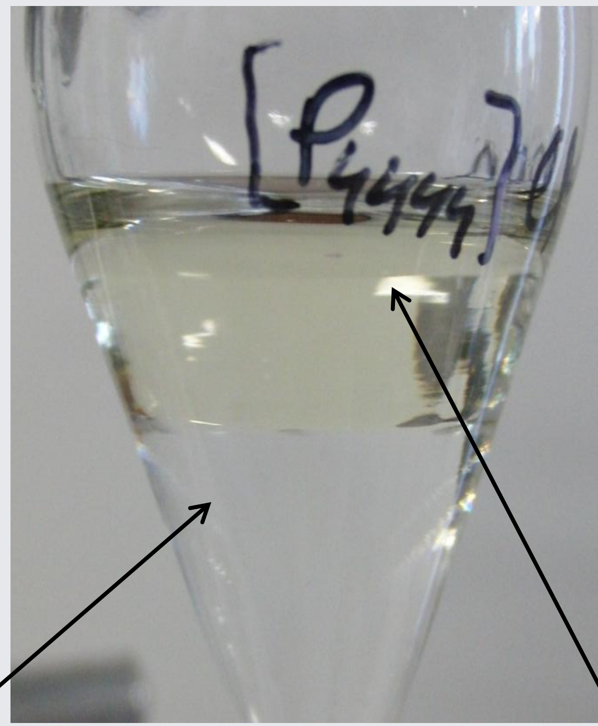
Aqueous Biphasic Systems (ABS)

for **Hydrophilic** ILs

- **Short processing time**
- **Biocompatible**



Salt – rich phase

IL – rich phase

- **Low energy consumption**
- **Readily scaled up**

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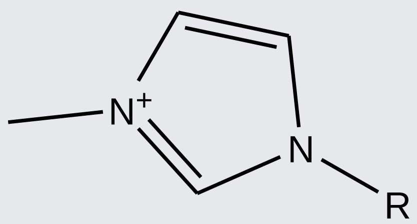
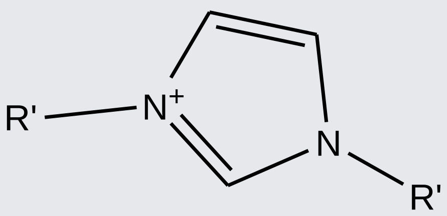
$C_nC_1$im series

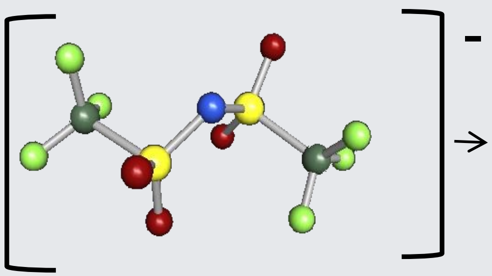


R = 1,2,3,4,5,6,8,12

$C_mC_m$im series



R' = 1,2,3



→ Based ILs

bis(trifluoromethylsulfonyl)amide ► $[NTf_2]^-$

Activated Charcoal

T = 308 K

3.2.1 Adsorption – Alkyl side chain length

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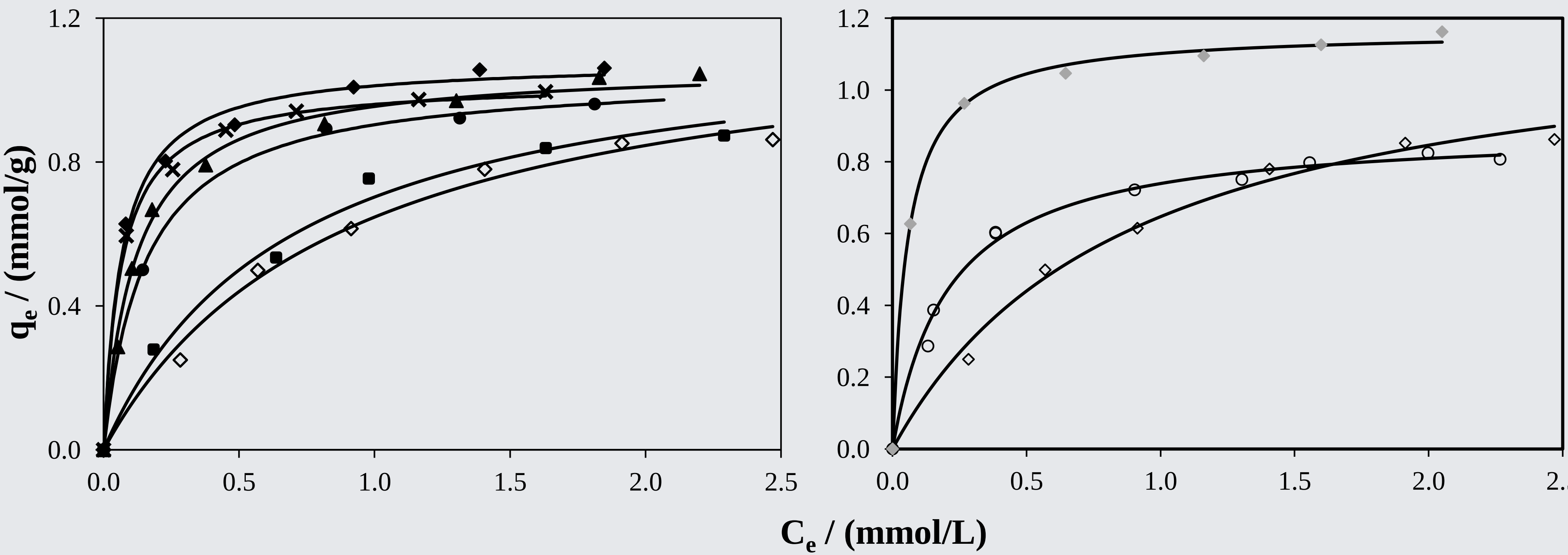
$C_nC_1$im series and $C_mC_m$im series:



(◊) [C_1C_1im], (■) [C_2C_1im], (•) [C_3C_1im], (▲) [C_4C_1im], (♦) [C_5C_1im], (×) [C_6C_1im]; (○) [C_2C_2im][NTf_2], (♦) [C_3C_3im][NTf_2]

C_nC_1im series and C_mC_mim series:

IL	K_d / (L/kg)
$[C_1C_1im]^+$	512.6
$[C_2C_1im]^+$	540.8
$[C_3C_1im]^+$	621.9
$[C_4C_1im]^+$	660.2
$[C_5C_1im]^+$	689.1
$[C_6C_1im]^+$	653.7
$[C_8C_1im]^+$	601.1
$[C_{12}C_1im]^+$	546.3

IL	K_d / (L/kg)
$[C_1C_1im]^+$	512.6
	545.9
	748.0

Higher adsorption

Decrease in adsorption

...tion coefficient

$\times$ 1000

$C_{e(=1.5\ mmol/g)}$

$[C_1C_1im]^+ < [C_2C_1im]^+ < [C_{12}C_1im]^+ < [C_8C_1im]^+ < [C_3C_1im]^+ < [C_6C_1im]^+ < [C_4C_1im]^+ < [C_5C_1im]^+$

$[C_1C_1im]^+ < [C_2C_2im]^+ < [C_3C_3im]^+$

3. Materials and Results

3.2.2 Adsorption – Isomers

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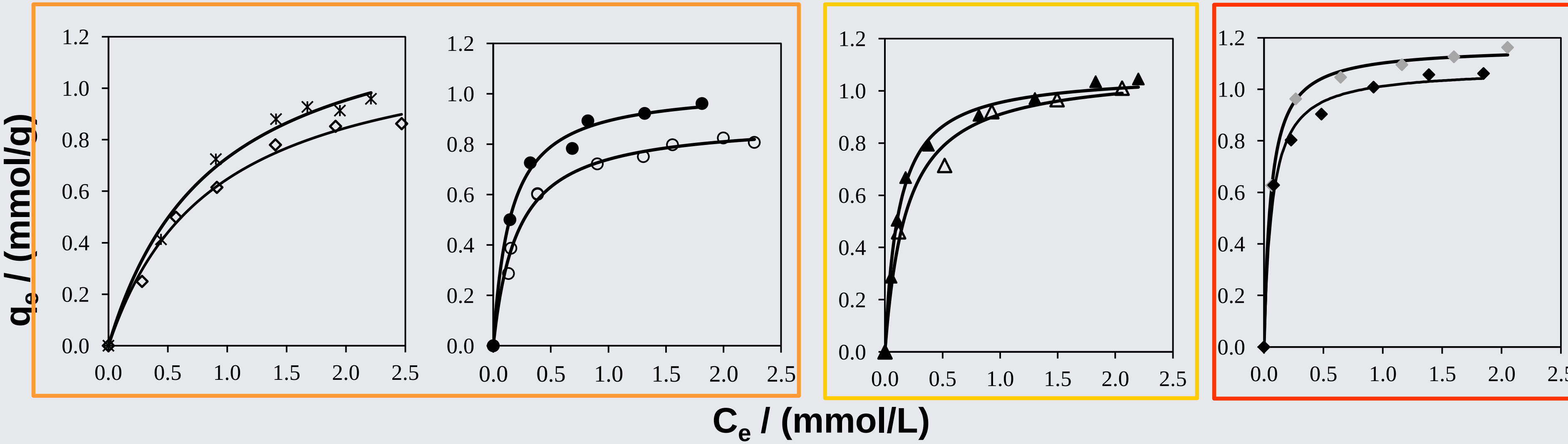
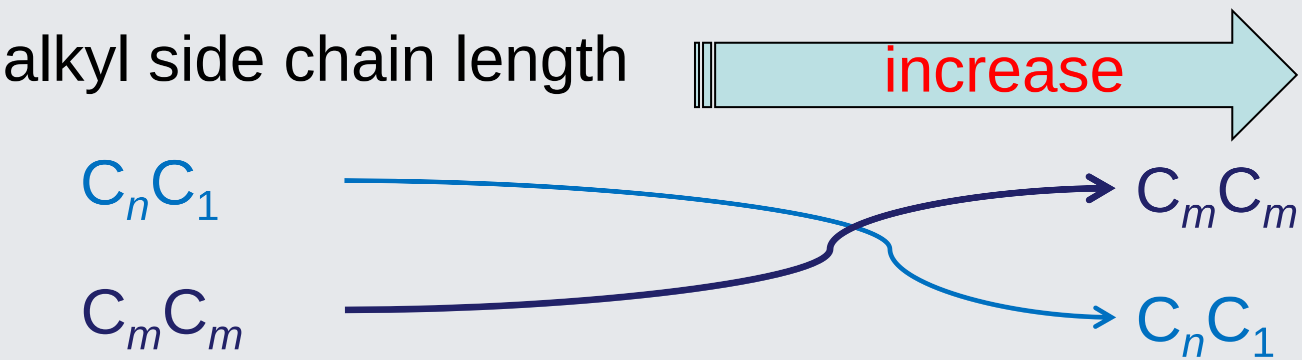
Comparison between $C_mC_m$im series and $C_nC_1$im series:

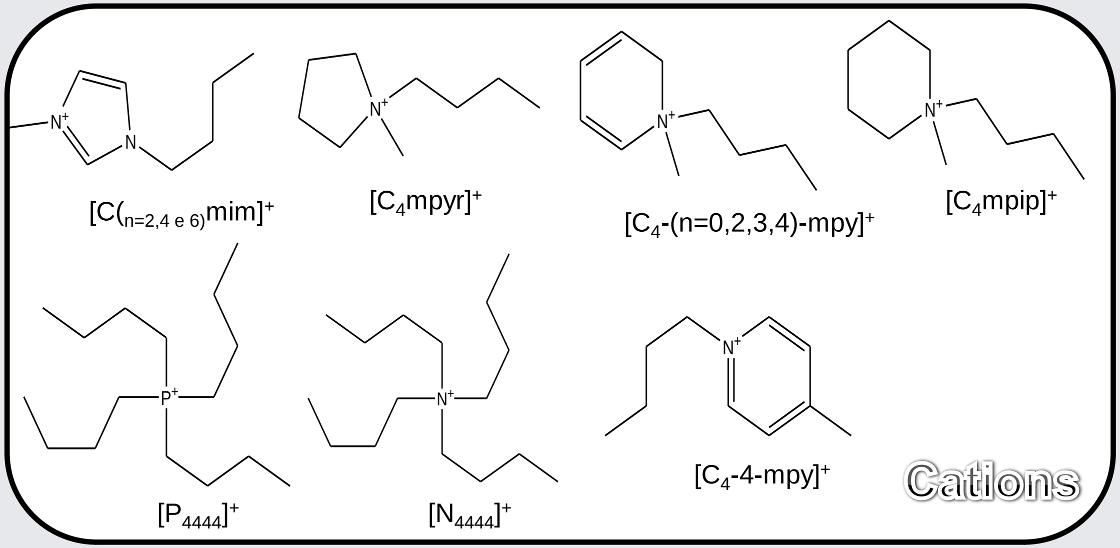


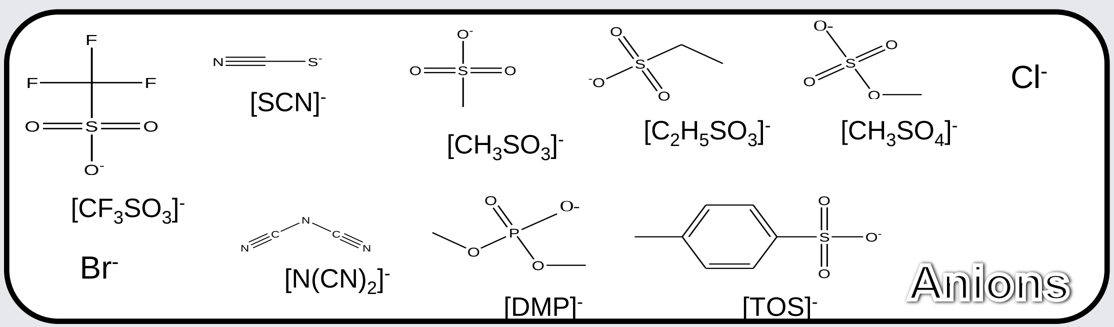
(⁎) [C_2im], (◊) [C_1C_1im]; b), (•) [C_3C_1im], (○) [C_2C_2im], (▲) [C_4C_1im], (△) [C_2C_3im], (♦) [C_5C_1im], (♦) [C_3C_3im].



3. Materials and Results

3.3 Materials- ABS



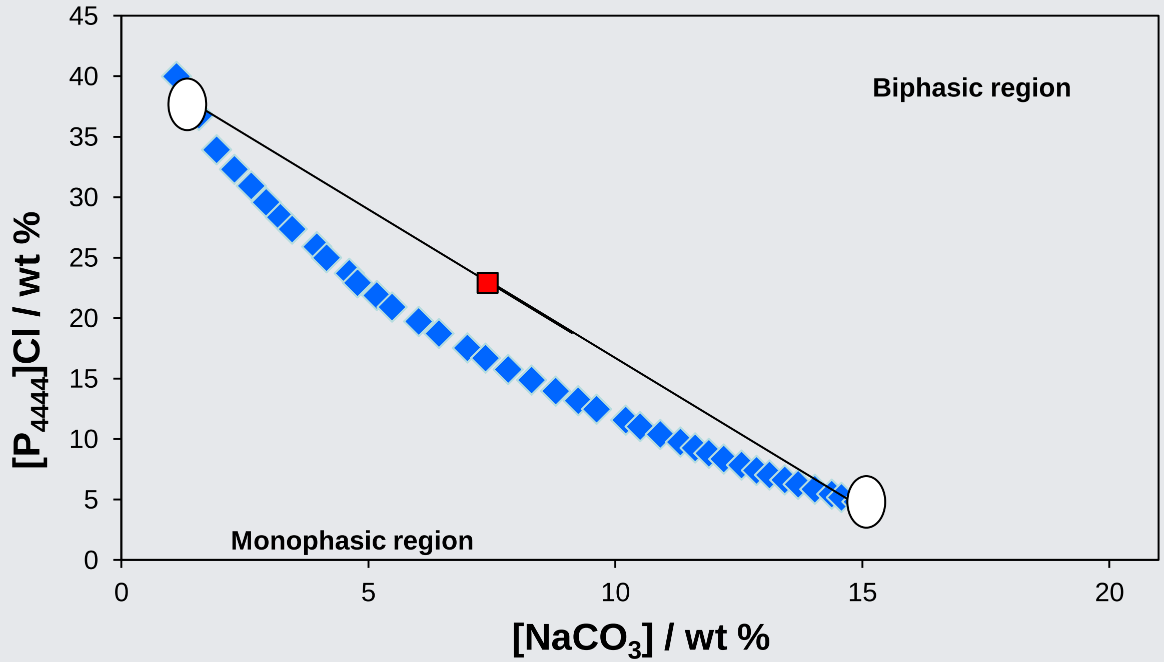


Na_2CO_3 as phase promoter agent due to its good salting-out ability

T = 298 K

3. Materials and Results

3.4.1 ABS – Measurements



$$[IL]_T = A \times e^{(B \times [Salt]_T^{0.5} - (C \times [Salt]_T^{3}))}$$

$$[IL]_B = A \times e^{(B \times [Salt]_B^{0.5} - (C \times [Salt]_B^{3}))}$$

$$[IL]_T = \frac{[IL]_M}{\alpha} - \frac{1-\alpha}{\alpha} \times [IL]_B$$

$$[Salt]_T = \frac{[Salt]_M}{\alpha} - \frac{1-\alpha}{\alpha} \times [Salt]_B$$

Mixture point → Two phases separation → Bottom and top phase weight → Calculation of the bottom and top weight fractions by the *Merchuk* equation

Merchuk, J. C.; Andrews, B. A.; Asenjo, J. A. J. Chromatogr., B 1998, 711, 285−293.

3. Materials and Results

3.4.2 ABS – Recovery efficiency

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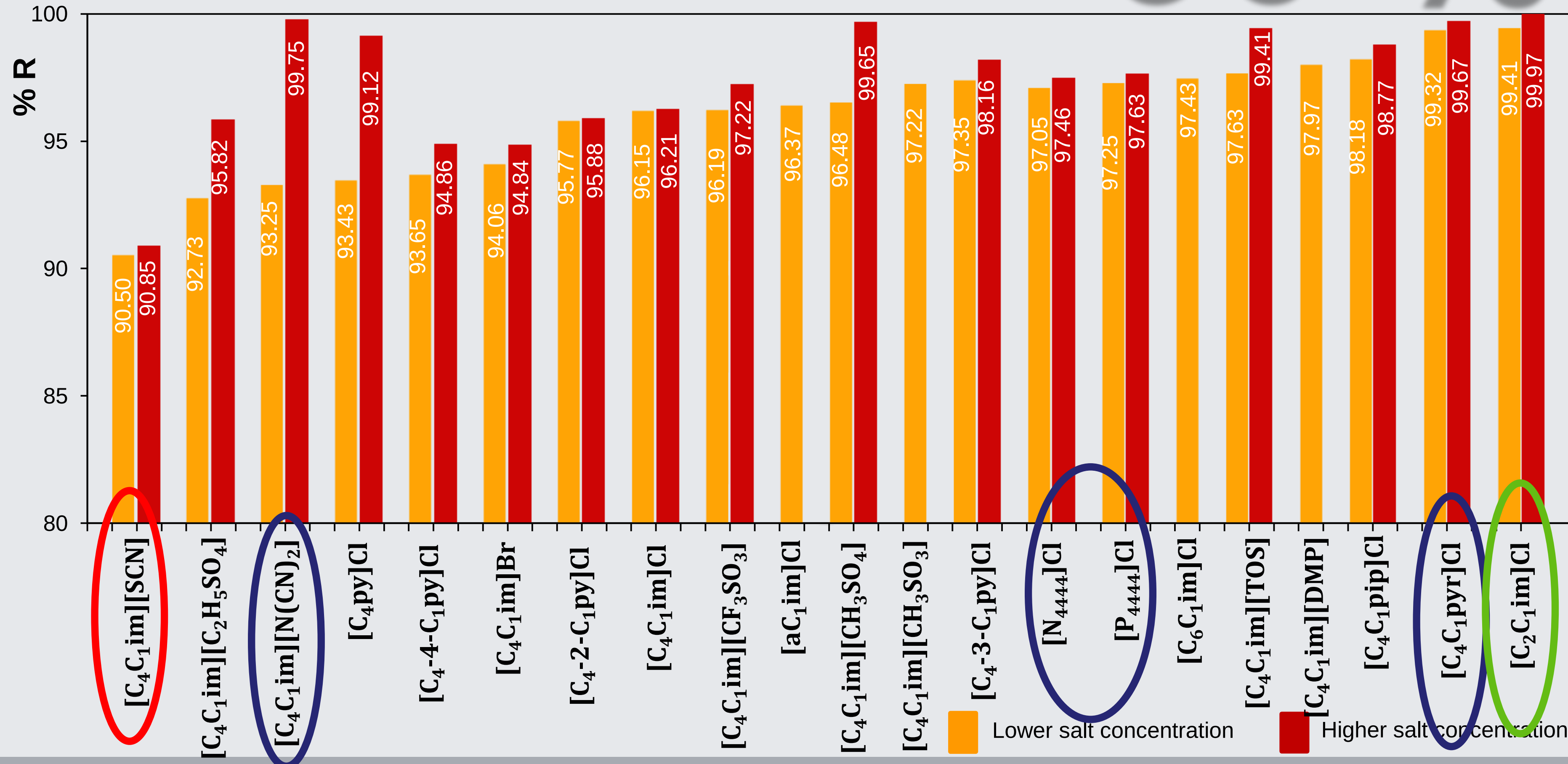
$$\%R = \frac{[IL]_{IL} \times m_{IL}}{[IL]_{IL} \times m_{IL} + [IL]_{Salt} \times m_{Salt}} \times 100$$

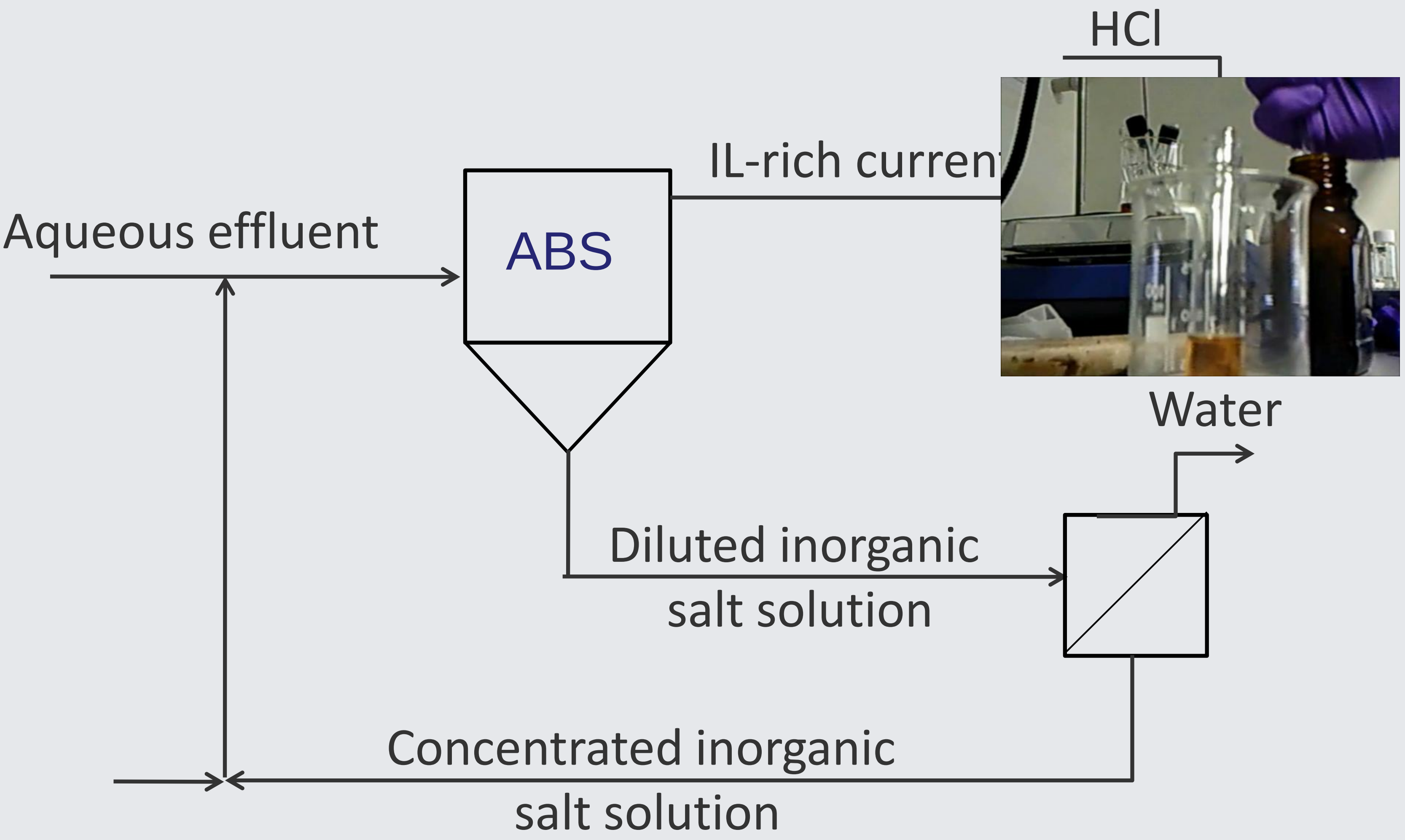
	Salt %	IL %
Range	3.4 – 14.0	[illegible]

> 90 %



3. Materials and Results

3.5 Process proposal



4. Conclusions

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Adsorption of ILs onto AC is **effective** at low concentrations.

Adsorption **increases** with the alkyl side chain length increase for both series studied.

Aqueous Biphasic Systems are a potential asset for the ILs Recovery. The recovery efficiencies obtained were **always higher than 90%**.

5. Future Work

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Adsorption:

- ❖ Recovery of ILs from AC (acetone*)
- ❖ ≠ anion families
- ❖ ≠ T e ≠ Adsorbents

ABS:

- ❖ Ionic exchange from the two salts
- ❖ ≠ salts with higher recovery efficiencies and low salt content

*J. Palomar, J. Lemus, M. A. Gilarranz, and J. J. Rodriguez, *Carbon, vol. 47, pp. 1846-1856, 2009.*

Acknowledgments