IMPACTS

The impact of the quality of $CO_2$ on transport and storage behaviour

$CO_2$QUEST

# IOLICAP Project Results

## Novel IOnic LIquid and supported ionic liquid solvents for reversible CAPture of $CO_2$- *IOLICAP*

Institute Nanoscience Nanotechnology

Ινστιτούτο Νανοεπιστήμης Νανοτεχνολογίας

George Romanos
Institute for Nanoscience and Nanotechnology
National Center for Scientific Research “Demokritos”

# Outline of the Presentation

## 4 major lines of Research

**Line 1** — Molecular Simulation

**Line 2** — Synthesis & Characterisation
Thermophysical Properties-Corrosion-Toxicity

**Line 3** — Development of Supported IL Absorbents and Membranes

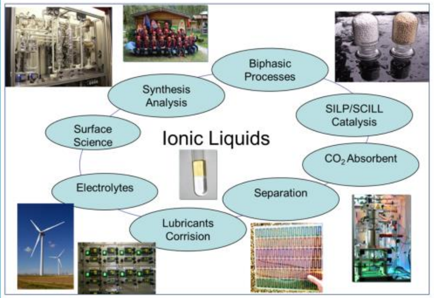
**Line 4** — Application of ILs in the Scrubbing/Stripping process

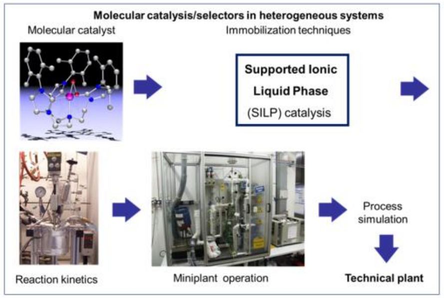
# Introduction of the Partners

## Synthesis of Ionic Liquids

FAU FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG

crt Lehrstuhl für Chemische Reaktionstechnik



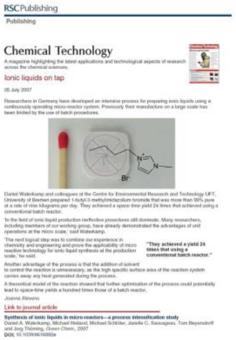


Prof. Peter Schulz


Prof. Peter Wasserscheid

- NMR-Self diffusivity
- Ion Chromatography
- Supported Ionic Liquids-Inverse SILPs
- Conductivity
- $CO_2$ solubility in bubble column reactors and high pressure volumetric cells

"They achieved a yield 24 times that using a conventional batch reactor."



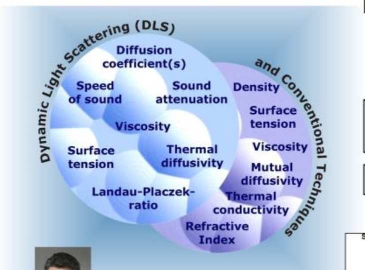

io·li·tec Ionic Liquids Technologies

Dr. Thomas Schubert
Dr. Boyan Iliev
Dr. G. Adamova


## Thermophysical/Physicochemical characterisation

FAU FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG

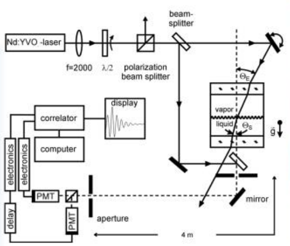
SAOT erlangen graduate school in advanced optical technologies



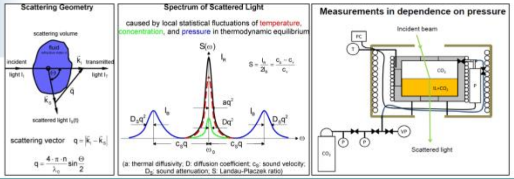


Prof. Andreas Paul Fröba


Prof. M. H. Rausch




temperature range: 230 - 400 K (ΔT ≈ ± 10 mK; temperature stability: < ± 1 mK)




- Mutual Diffusivity with Dynamic Light Scattering
- Viscosity and Surface Tension by Surface Light Scatttering
- $CO_2$ solubility by bubble point pressures and gravimetric analysis
- Kinetics of sorption-gravimetric

TU/e Technische Universiteit Eindhoven University of Technology

- Chair: Prof. dr. ir. Maaike C. Kroon
- Prof. dr. ir. Cor J. Peters

$CO_2$ Solubility Equilibria / kinetics gravimetric measurements


Magnetic Suspension Balance

$CO_2$ Solubility Equilibria: bubble point pressures

Cailletet tube

Windowed autoclave equipment

Vapor/Liq. Equilibria


VLE: Ebulliometer

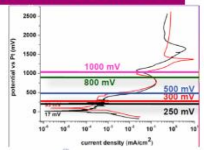
# Introduction of the Partners

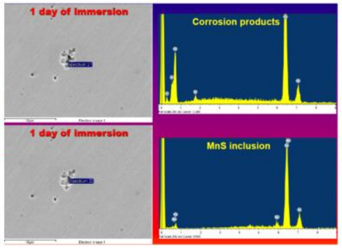
## Corrosion

MANCHESTER 1824 Advanced methods for evaluating the corrosion properties of ILs / corrosion inhibition.

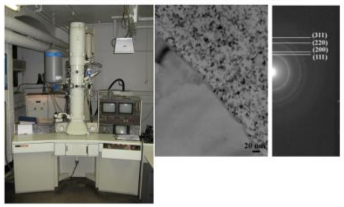
**Materials**
**Mild steel (MS), stainless steel of types 304 and 316**

- Immersion tests for several days
- Potentiodynamic and potentiostatic tests

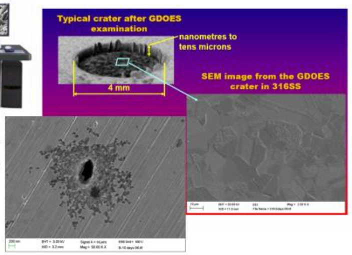



JEOL TEM 200FX II transmission electron microscope with electron diffraction facilities



Zeiss Ultra 55 scanning electron microscope with EDX and BSD facilities-Study of corrosion products.



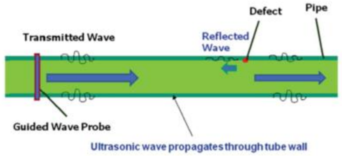

Prof George Thompson

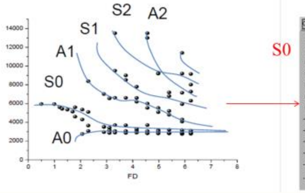
*•Advanced microscopy techniques for examining corrosion of materials*
*•Potentiodynamic and potentiostatic tests*
*•Guided surface waves for on-line monitoring corrosion in vessels*

ENDITECH s.a. DESIGN & APPLICATIONS

Dr. G. Diamantopoulos
Ms. V. Zatta

1. Structural radar
2. Monitoring
3. Faster
4. Applicable to inaccessible areas





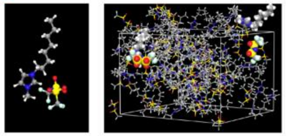
## Molecular Design

- Development and validation of accurate force fields
- Study of the molecular mechanisms and calculation of macroscopic properties
- GCMC simulations of gas absorption in graphitic materials
- Develop a suitable EoS model for the phase behaviour of ILs/gas systems

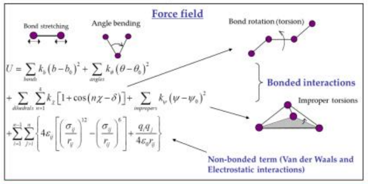
Dr. Ioannis Economou

SCIENOMICS delivering science

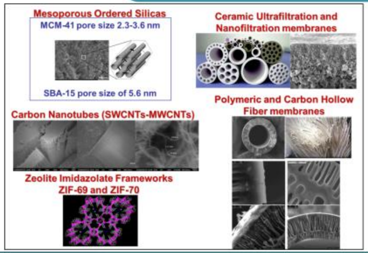
Dr. X. Krokidis Dr. J-R. Hill



Ion pairs of [C8mim+][Tf2N-] Molecular model of ionic liquid

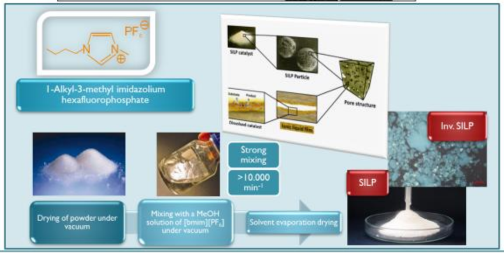



## Development of SILPs and SILMs



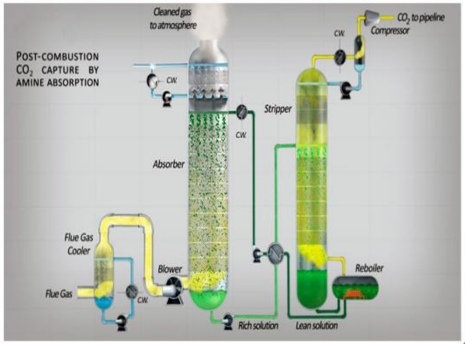

Dr. G. Romanos


IGA (0-20 bar)

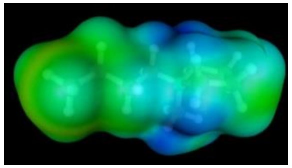


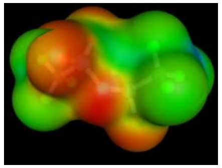

## Process Development and Engineering

N & K ΓΚΟΛΙΟΠΟΥΛΟΣ
ΑΝΩΝΥΜΗ ΤΕΧΝΙΚΗ ΕΤΑΙΡΕΙΑ

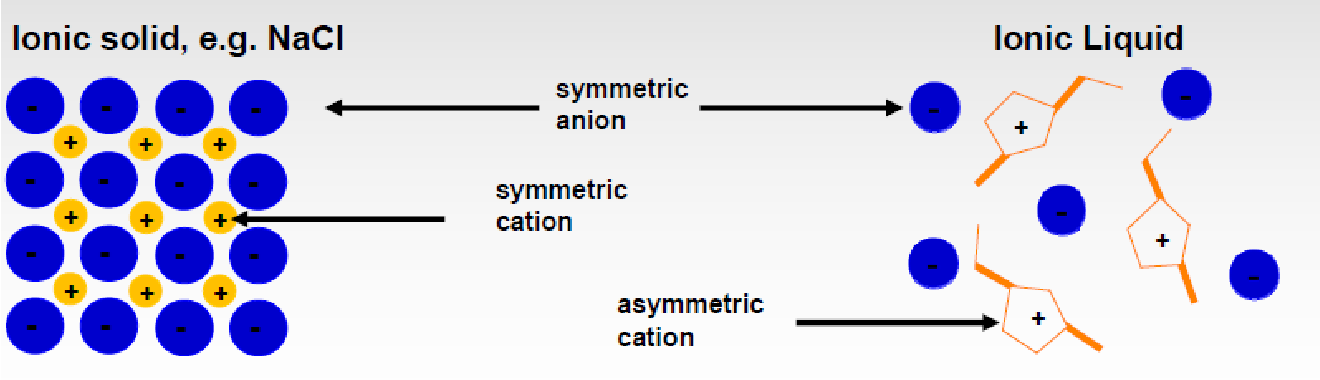


# What are Ionic Liquids?





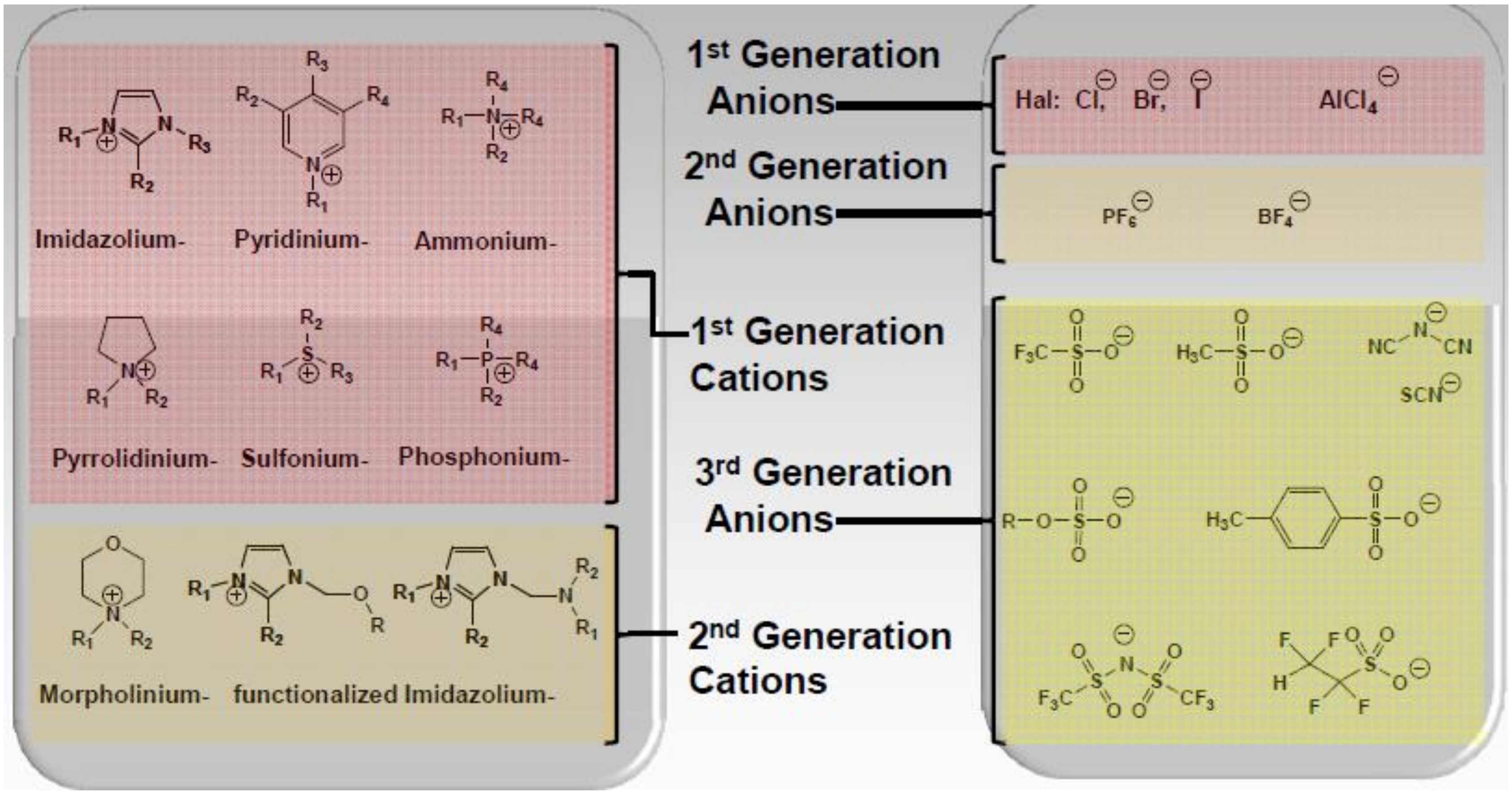
“Ionic Liquids is the generic term for a class of materials, consisting entirely of ions and being liquid below 100°C.”
“If they are liquid at room temperature, we call them (RTILs).”




- Weak coordinating tendency of the ion pair.
- Low intermolecular interaction.
- Breaking the symmetry of its chemical structure.

# Generations of cations and anions

ILs are now about 100 years old, when ethylammonium nitrate was found to be liquid under ambient conditions.



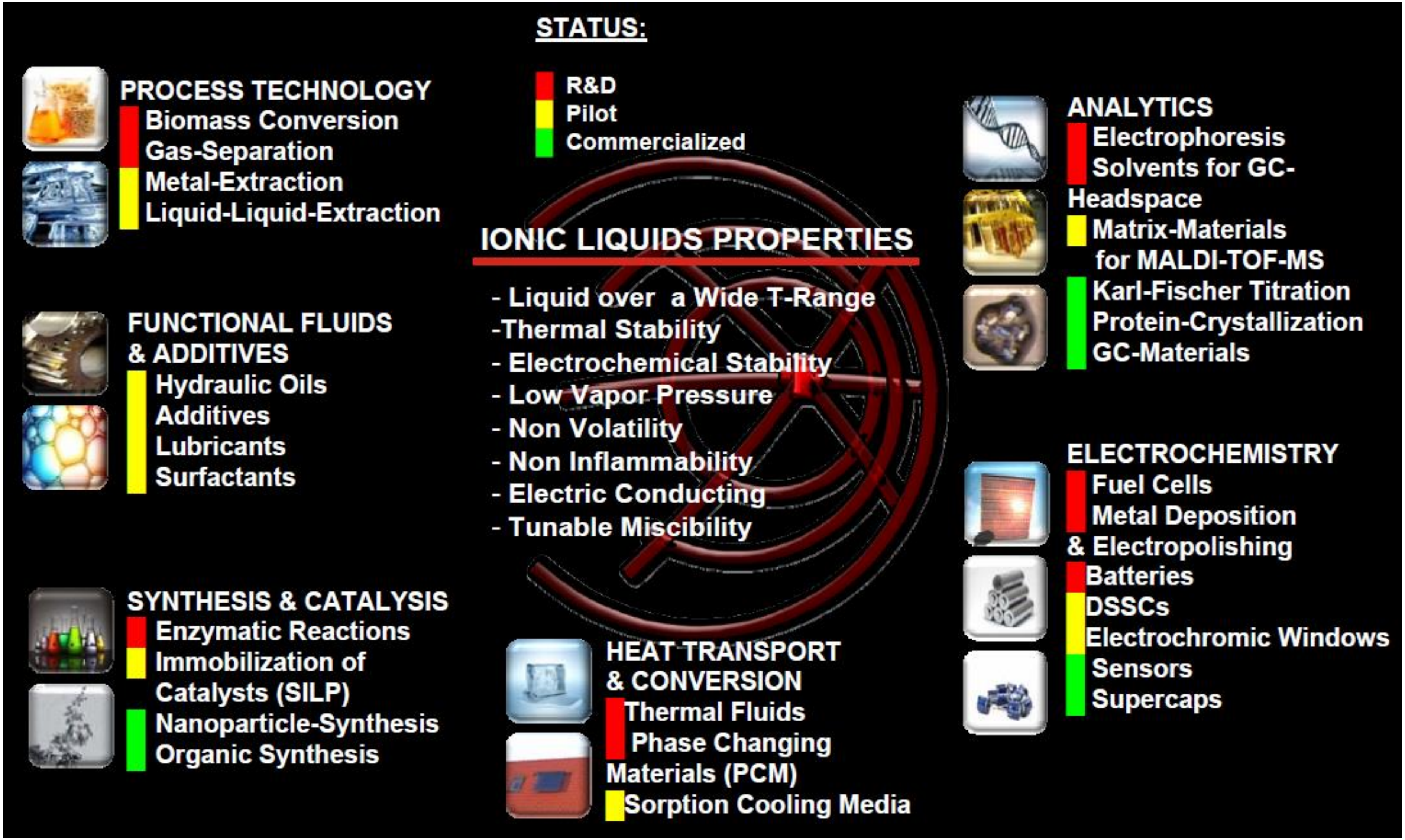
# Properties



- Very good solvents properties for a wide variety of organic, inorganic and organometallic compounds
- High thermal and chemical stability
- High electrical conductivity
- Low vapor pressure
- Large electrochemical window
- Fine-tuning the structure, these properties can be tailor-designed
- High solubility of gases especially $CO_2$

# Applications





# ILs *vs* amines

They can be used as solvents for $CO_2$ capture?

## •Disadvantages compared to amines

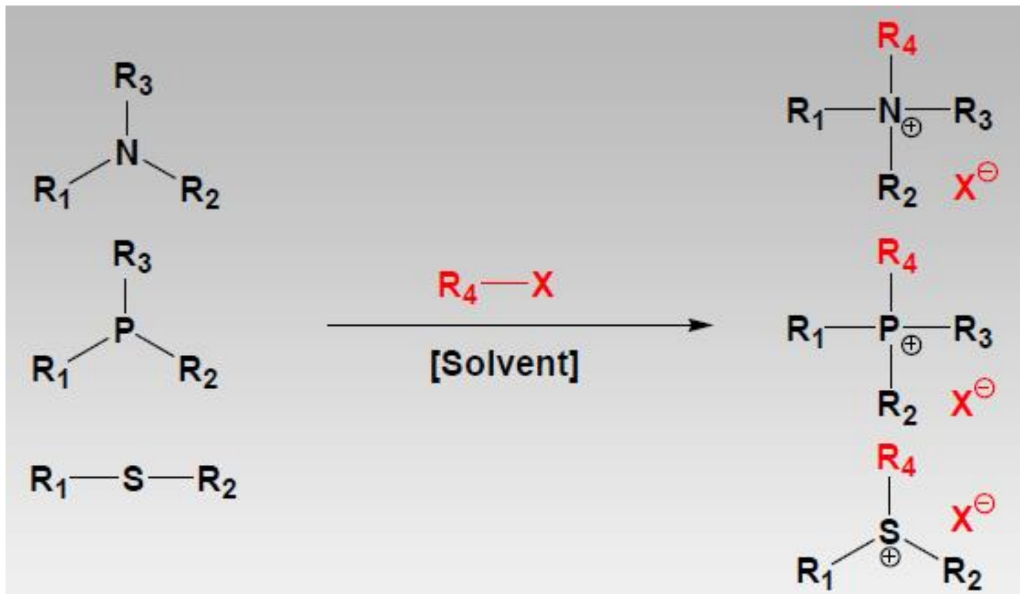
**Viscosity** @ RT – 15-500cP

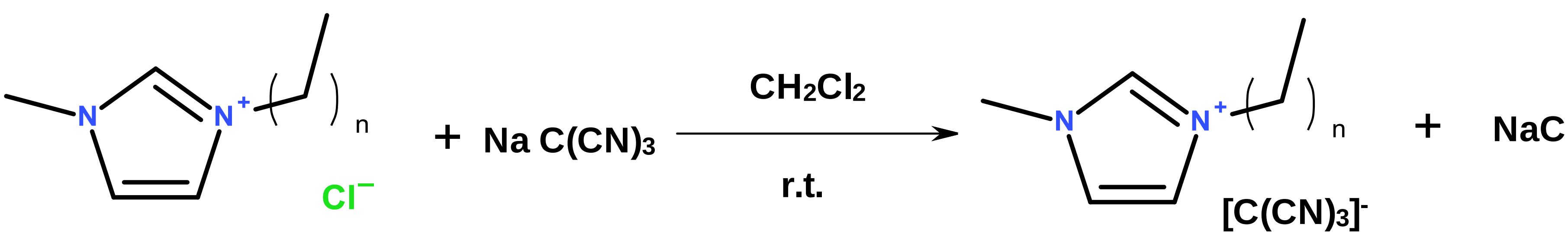
**Physisorption**---$CO_2$ absorption capacity < 0.05 mol/mol at 1 bar

**Binary $CO_2$/IL diffusivity** – $10^{-11}$ to $10^{-9}$ $m^2$/sec

**Cost** – 100-200€ at the 100kg level

# Alkylation Reaction



# Reasons for their high cost



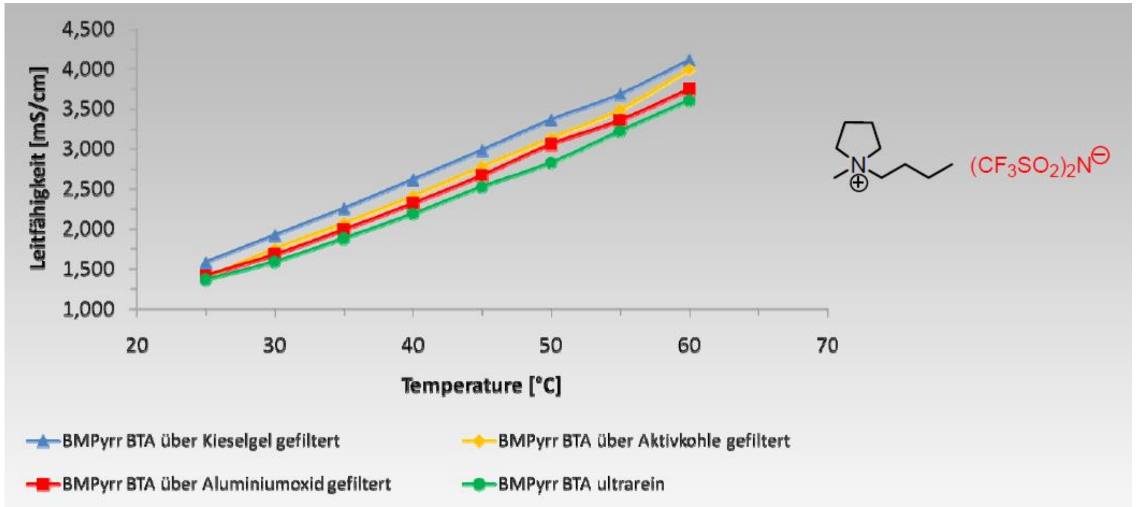
- Very good solvents properties for a wide variety of organic, inorganic and organometallic compounds.

One way to reduce the cost

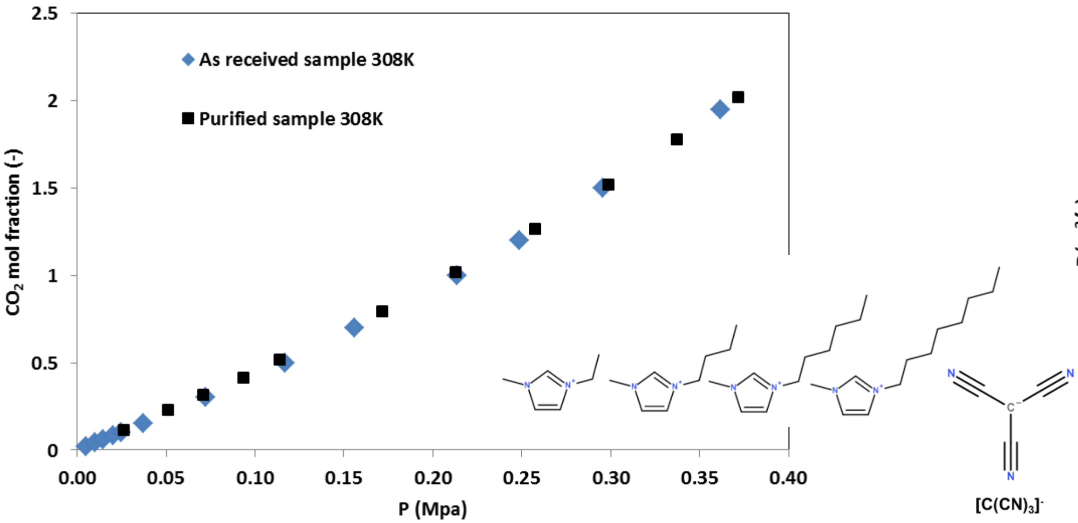
Have the impurities any effect on the properties of interest?

# Example

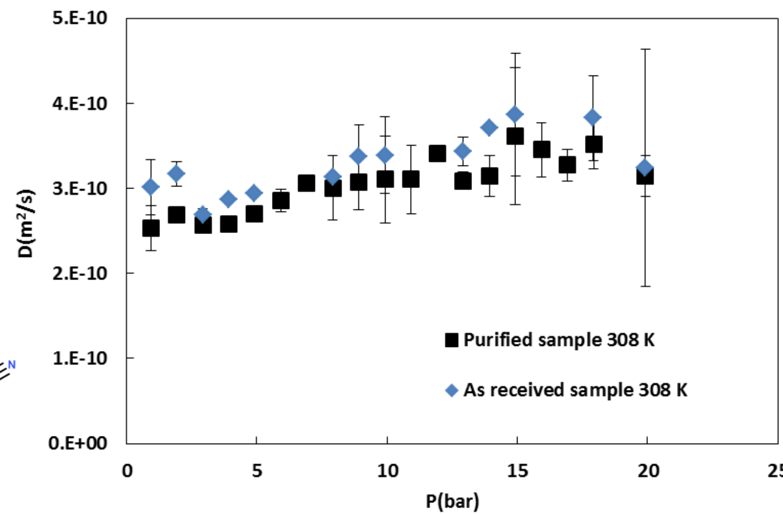
## Conductivity? Y



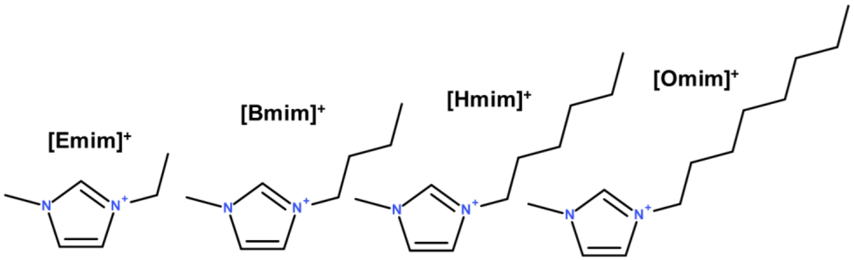

## $CO_2$ Solubility? N

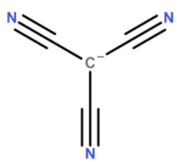



## Binary $CO_2$/IL diffusivity? N



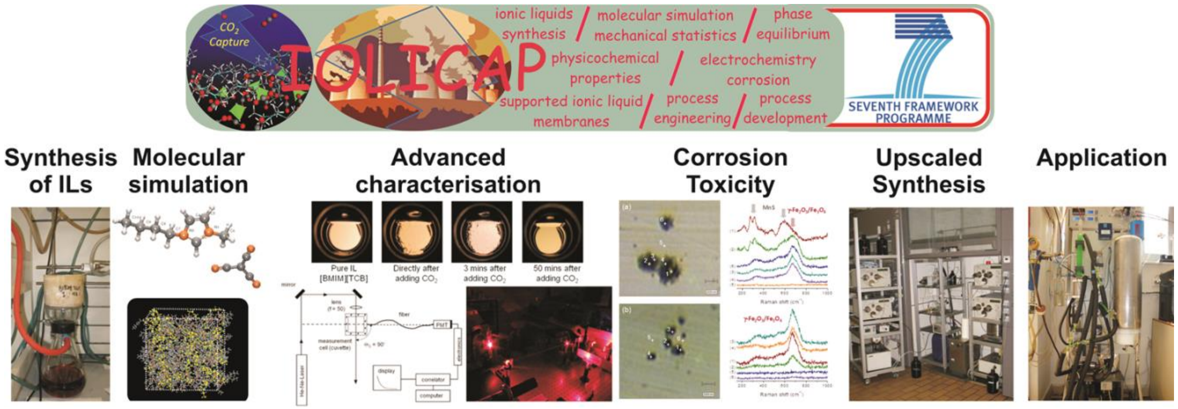
# High Scale production at low cost

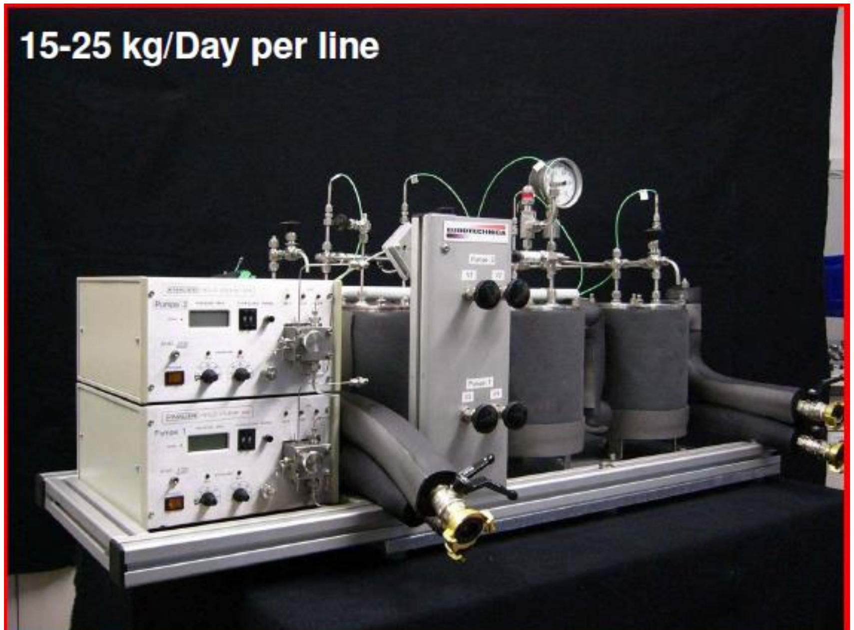


$[C(CN)_3]^-$

## IOLICAP PROJECT



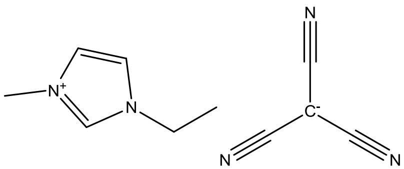




Iolitec Company used a continuous flow microreactor technology to synthesise 200 kg of the most promising ILs for $CO_2$ capture at a cost of

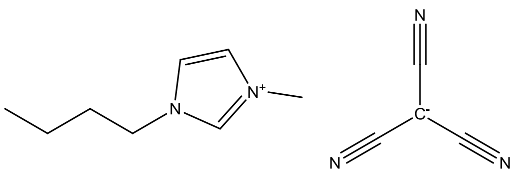
100 € per kg.

# Ionic Liquids examined within IOLICAP

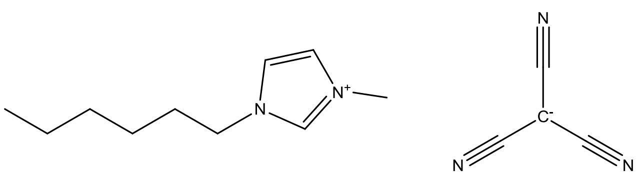
## TCM-based ILs



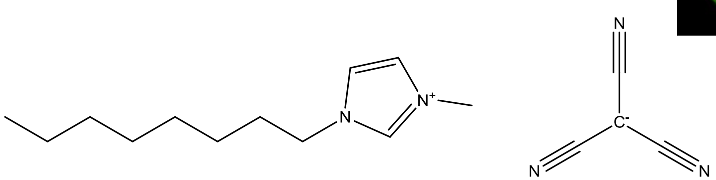
1-ethyl-3-methylimidazolium tricyanomethanide



1-butyl-3-methylimidazolium tricyanomethanide

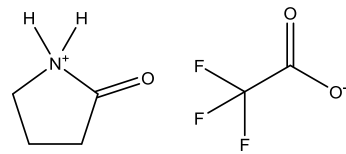


1-hexyl-3-methylimidazolium tricyanomethanide

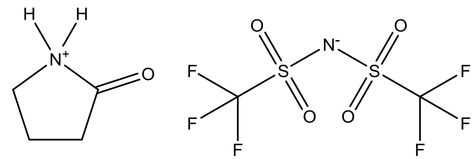


1-octyl-3-methylimidazolium tricyanomethanide

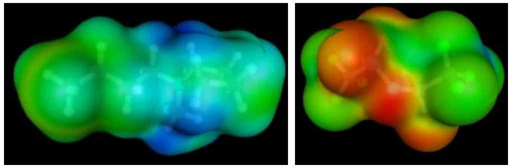
## Lactam-based ILs



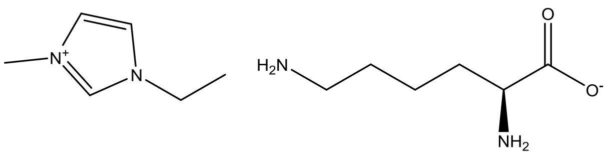
pyrrolidium-2-one trifluoroacetate



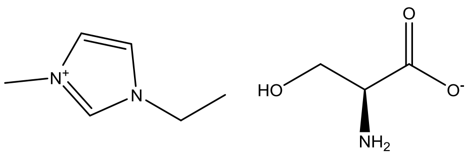
pyrrolidium-2-one bis(trifluoromethylsulfonyl)imide



## Amino acid-based ILs

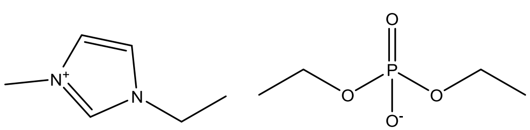


1-ethyl-3-methylimidazolium lysinate

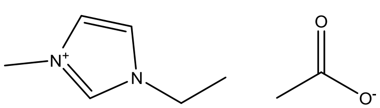


1-ethyl-3-methylimidazolium serinate

## Acetate and Phosphate anions

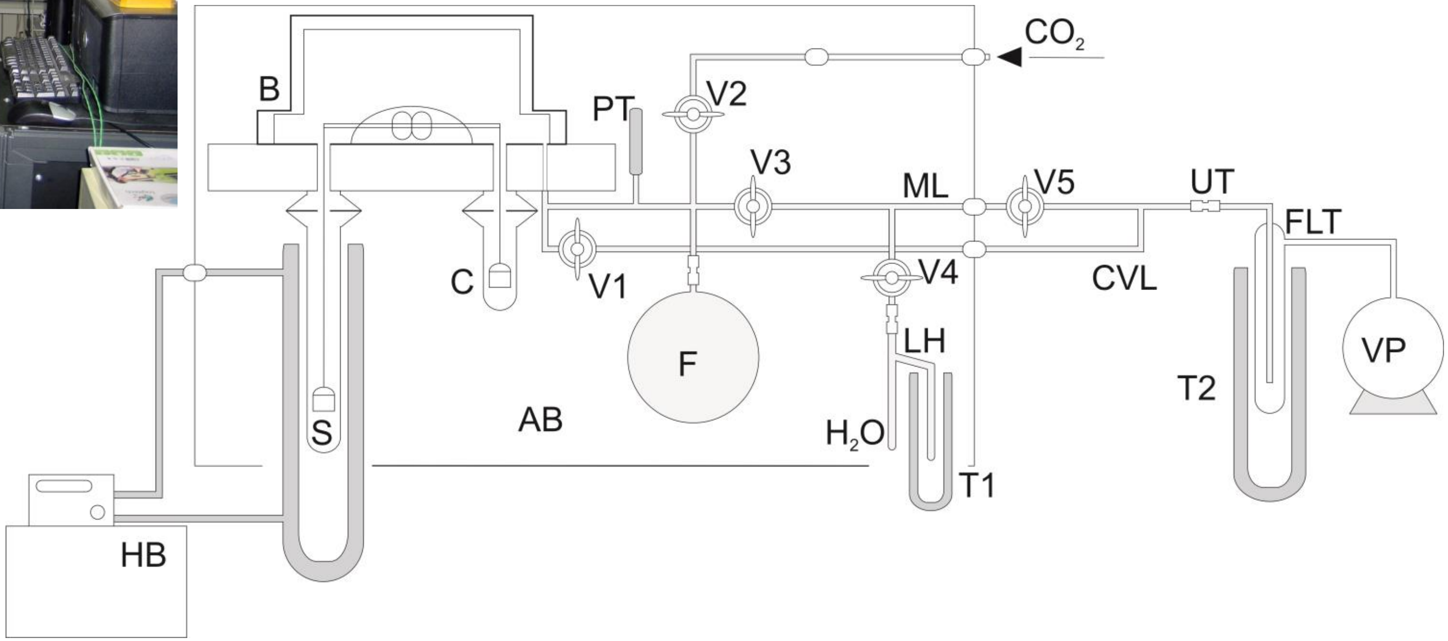


1-ethyl-3-methylimidazolium diethylphosphate



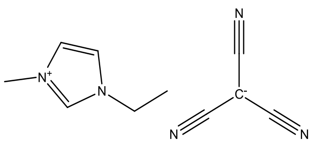
1-ethyl-3-methylimidazolium acetate

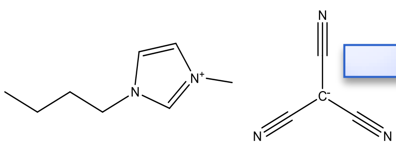
# Effect of water on the $CO_2$ solubility and diffusivity of ILs with the gravimetric technique

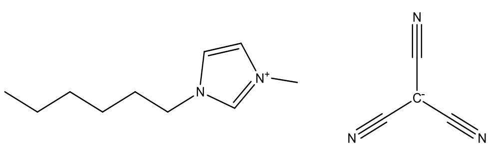



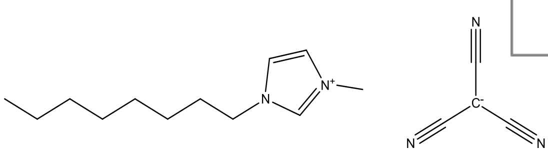
# Effect of water on the $CO_2$ solubility of ILs

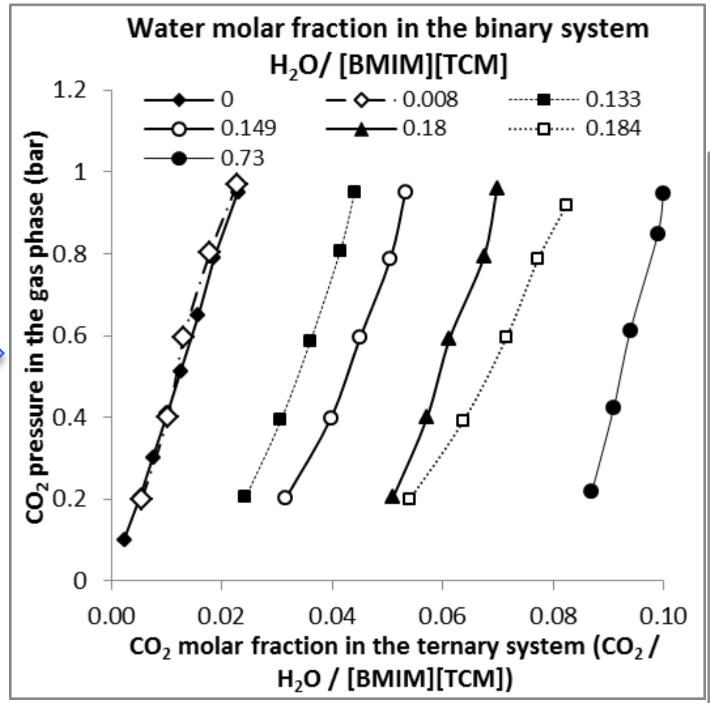
**TCM-based ILs**

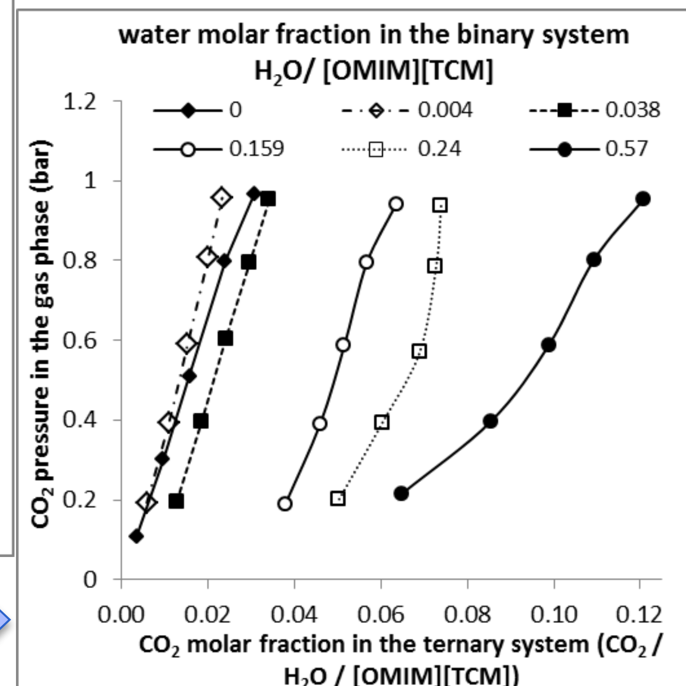

1-ethyl-3-methylimidazolium tricyanomethanide


1-butyl-3-methylimidazolium tricyanomethanide


1-hexyl-3-methylimidazolium tricyanomethanide

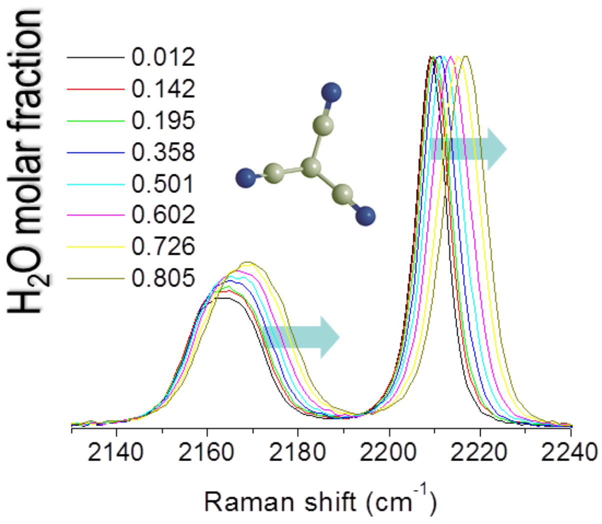

1-octyl-3-methylimidazolium tricyanomethanide

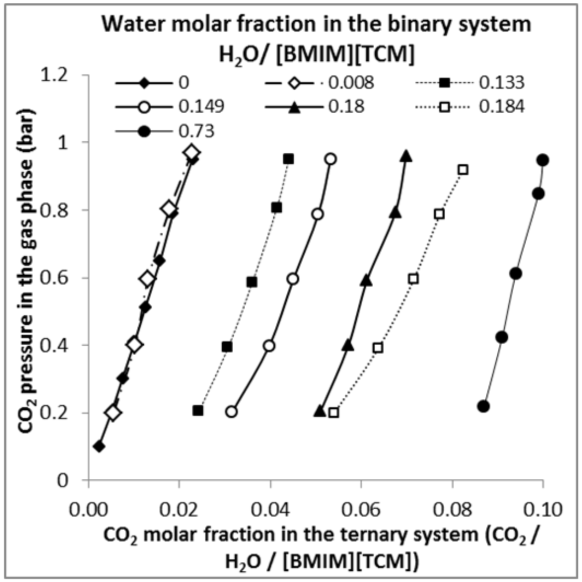


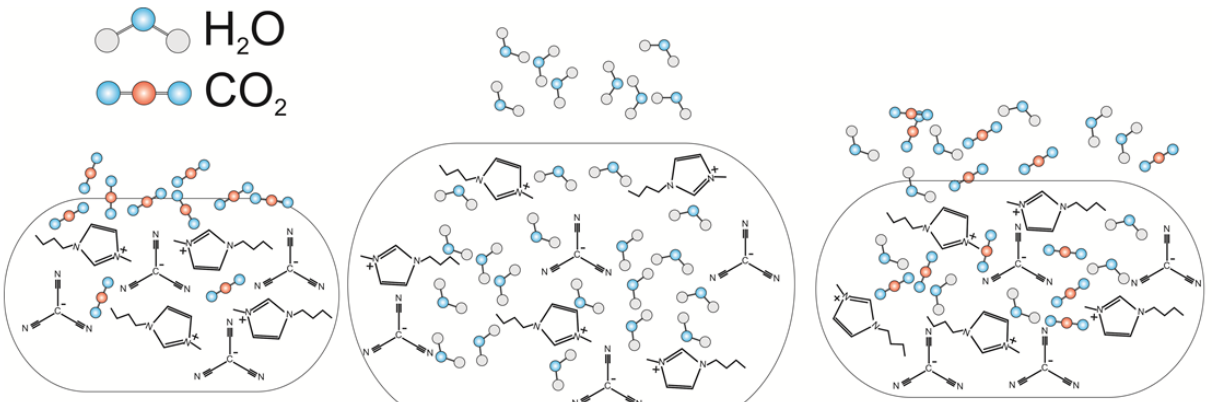



# IOLICAP-Results

## $[C_nC_1im][C(CN)_3]-H_2O-CO_2$



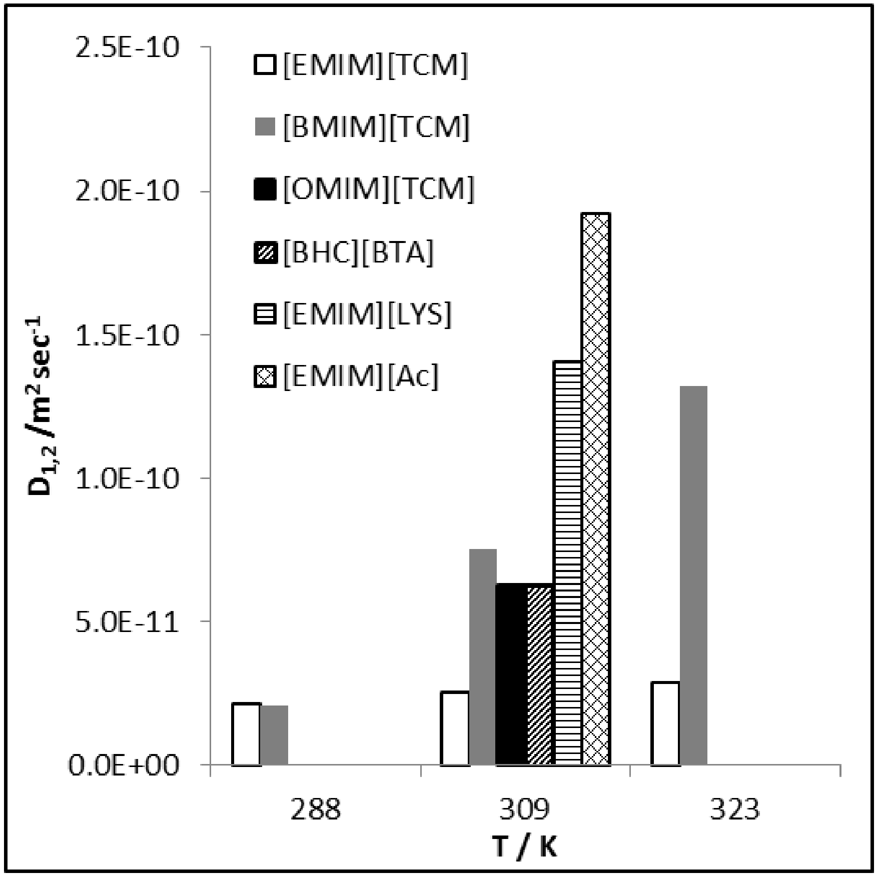



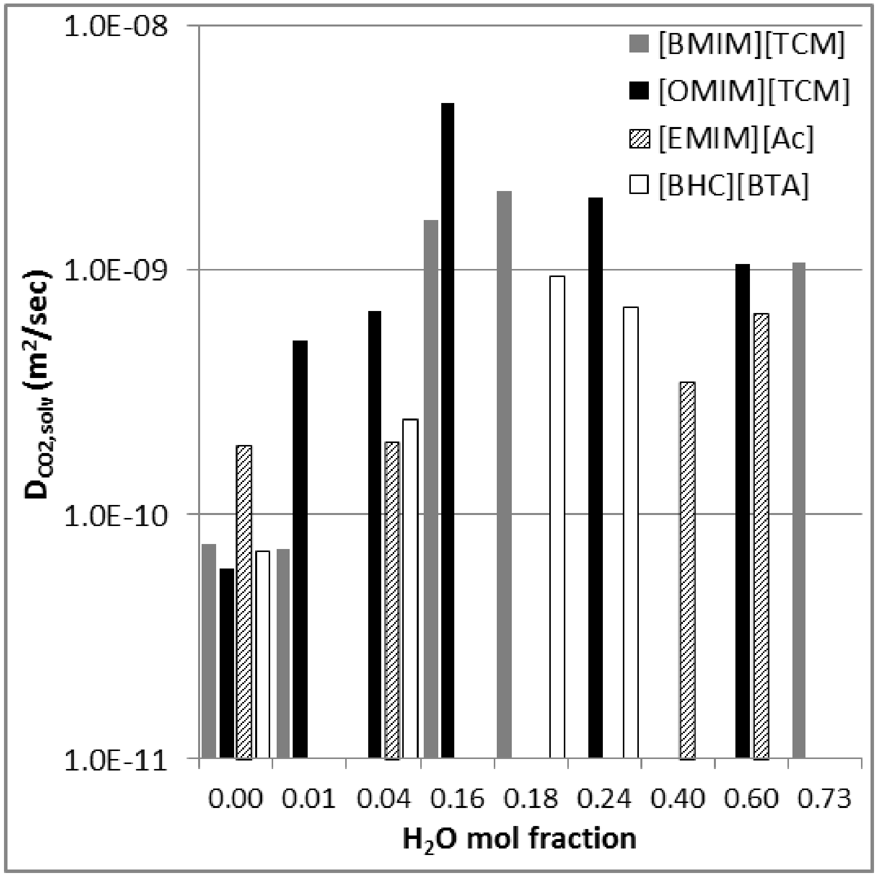

dry IL

Volume expansion-weakened cation/ anion interaction

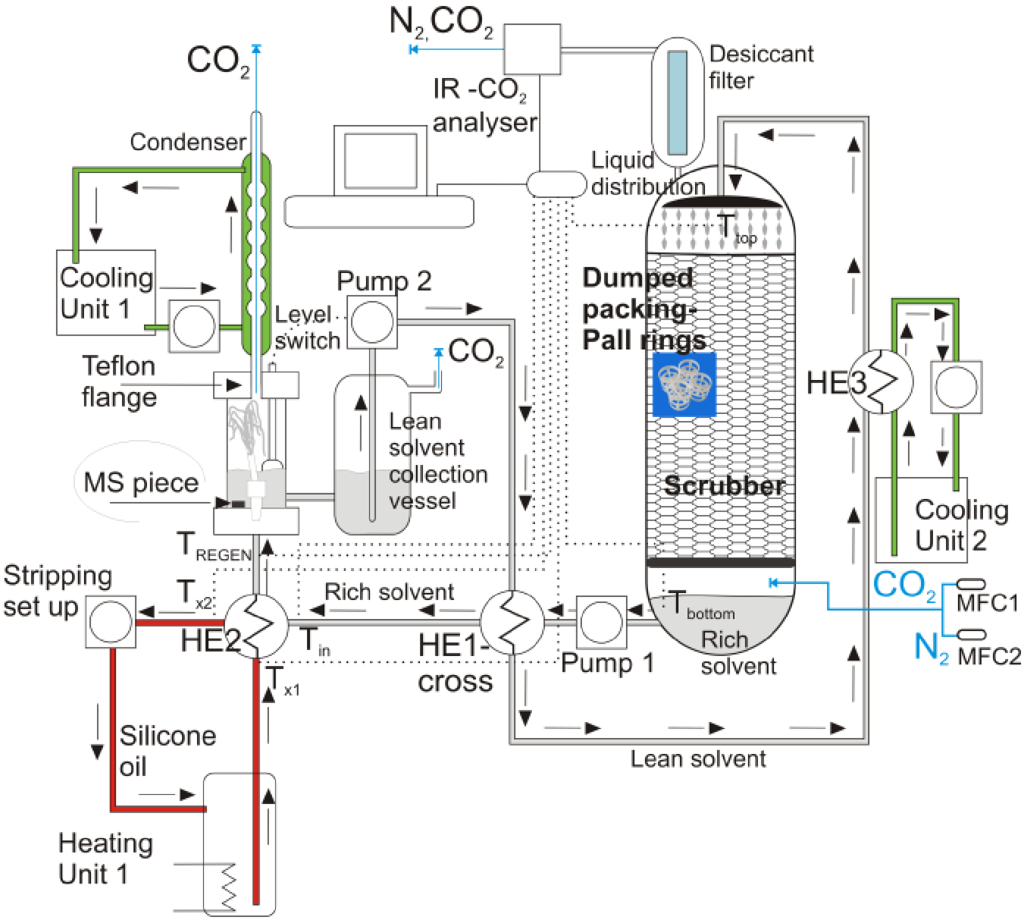
Exchange water/$CO_2$
system returns to initial state but with more $CO_2$ molecules absorbed

# Effect of water on the $CO_2$ diffusivity of ILs

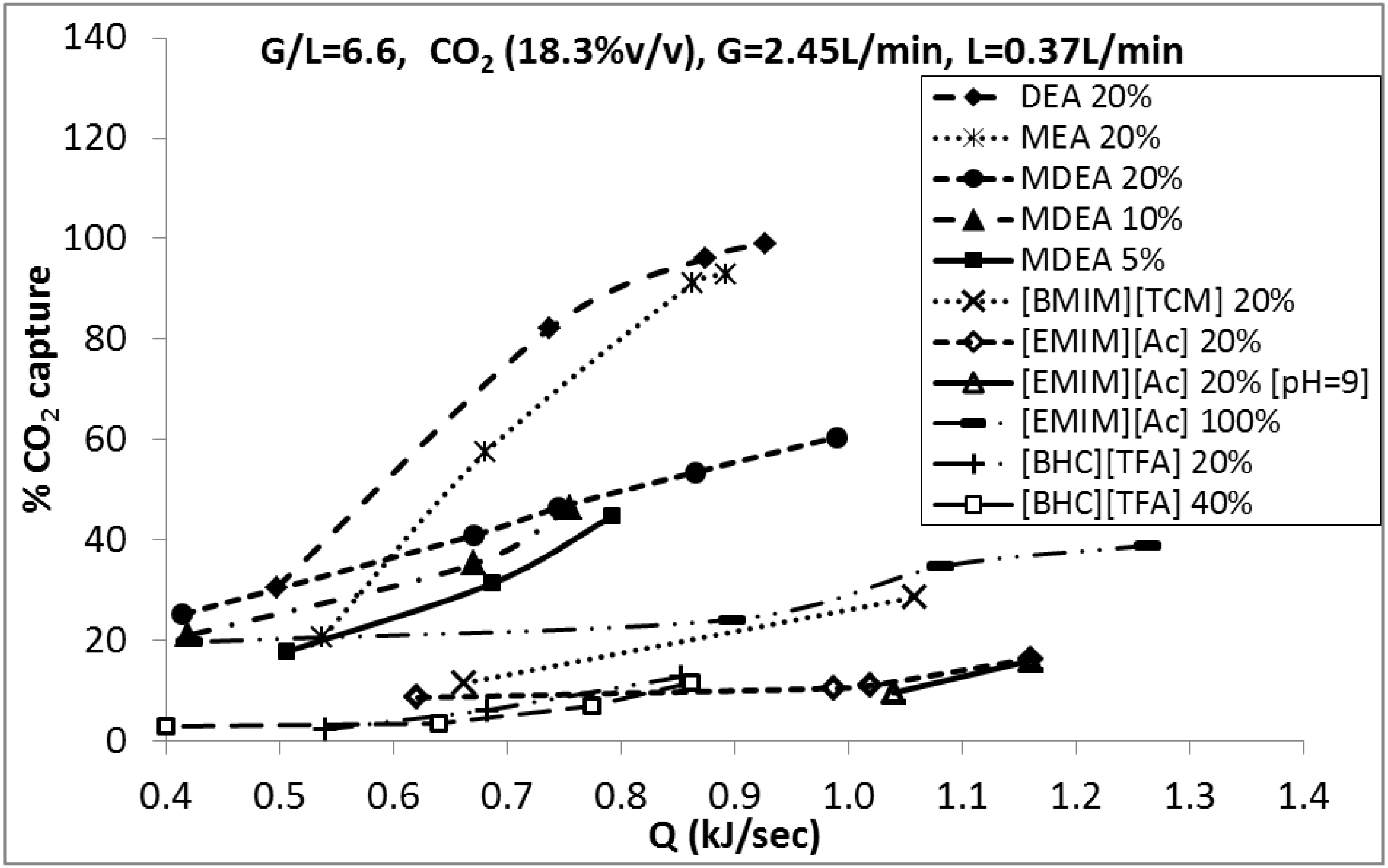


# Is this enough?
# Perform tests in a scrubbing/stripping device

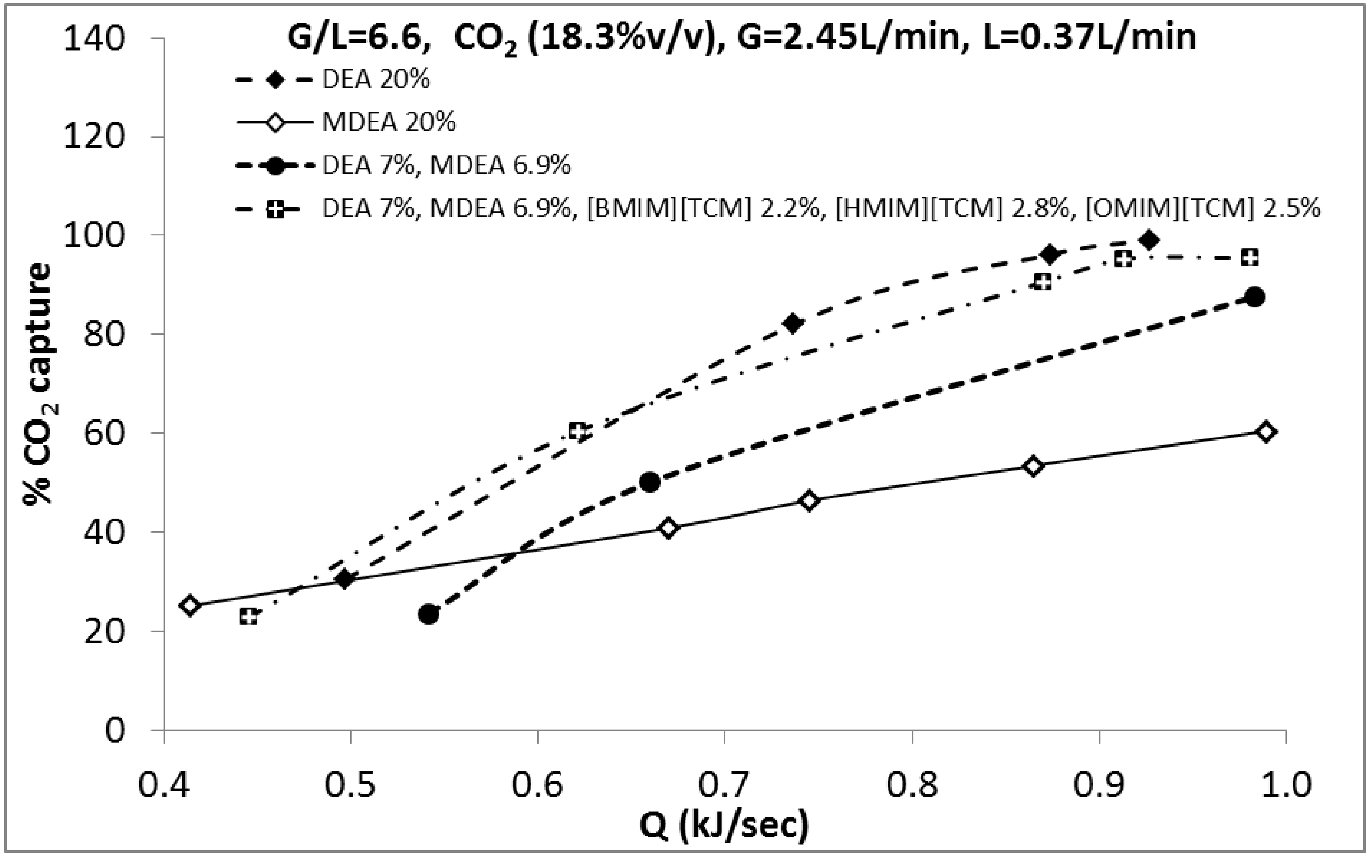



# ILs could not compete with amines
# Slow capture kinetics the major problem



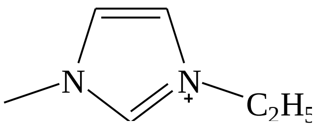
# IOLICAP-Results

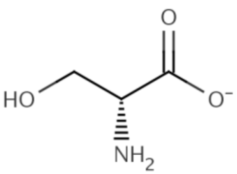
## Use them in mixture with amines.
## Try to reduce amine content.

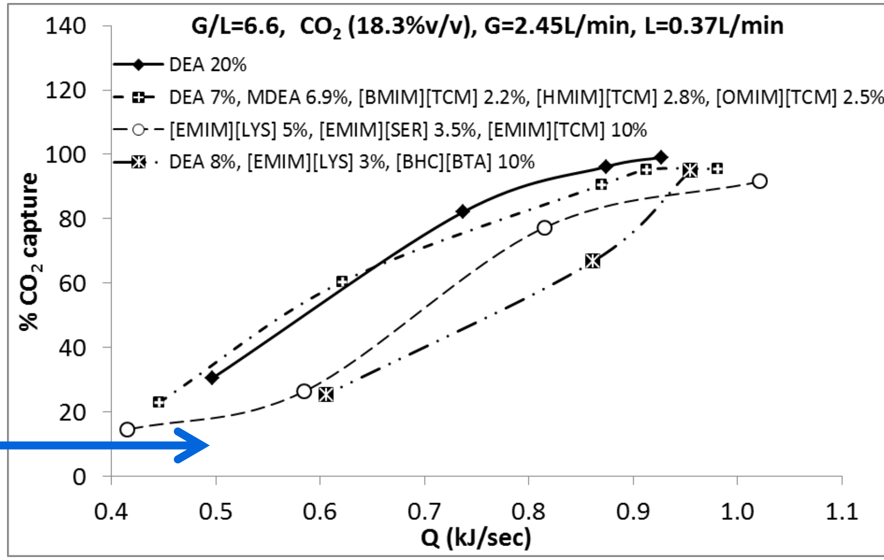


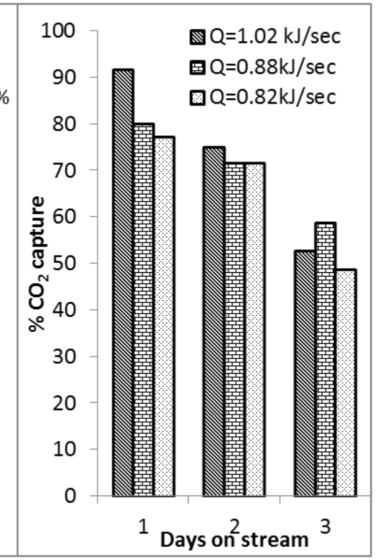

A mixture consisting of 7% DEA, 6.9% MDEA and 7% ILs had the same efficiency with the 20% DEA solution

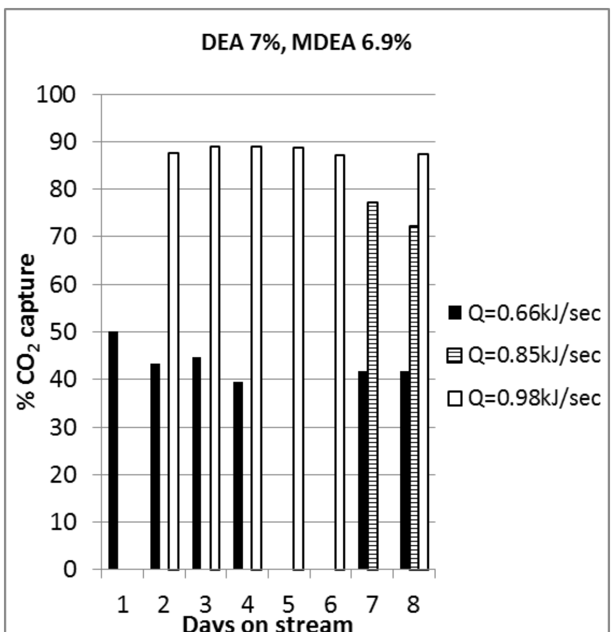
# IOLICAP-Results

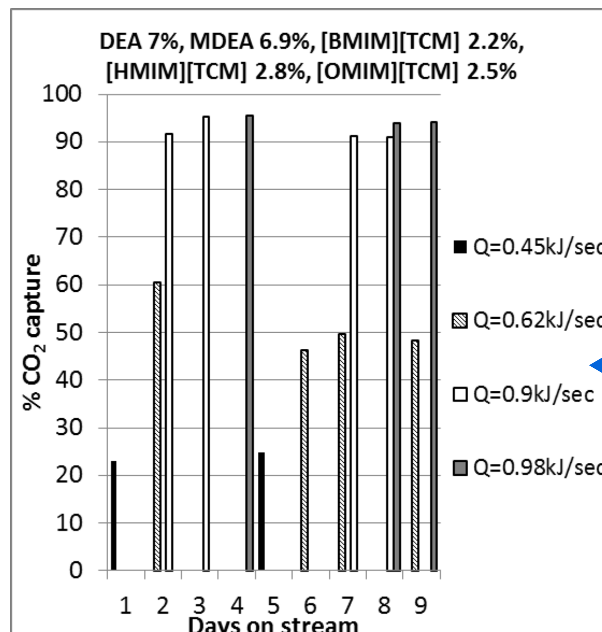


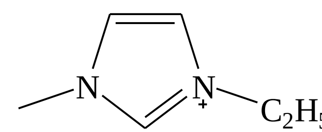



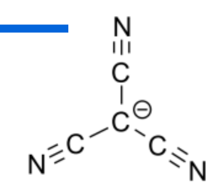



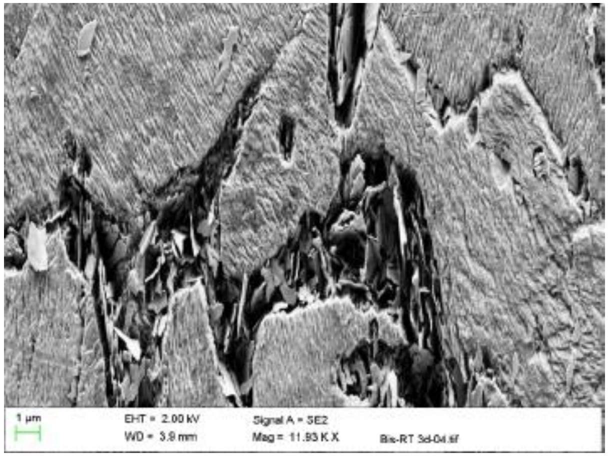



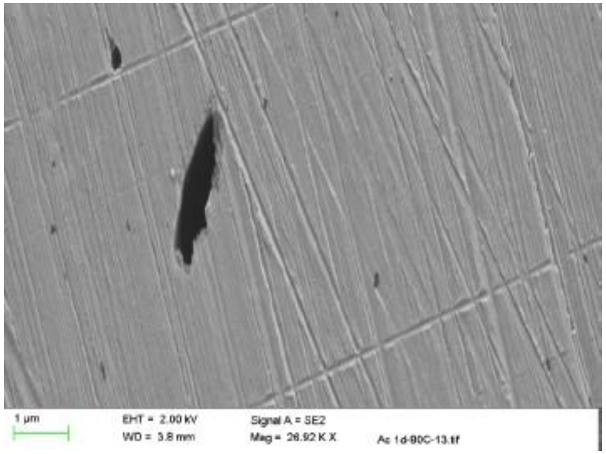



# Less Corrosive for Mild Steel




7% DEA, 6.9% MDEA

attack severely the surface of mild steel, leading to dissolution of metal over the entire surface and significant weight loss

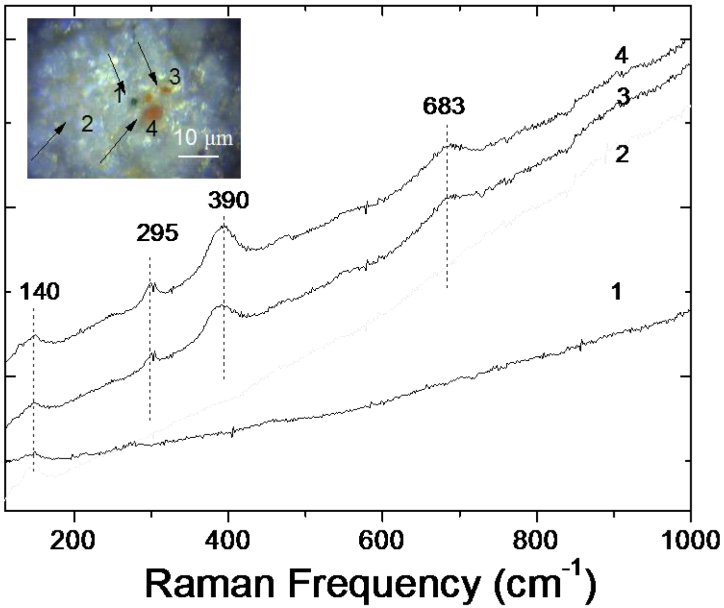



7% DEA, 6.9% MDEA and 7% ILs

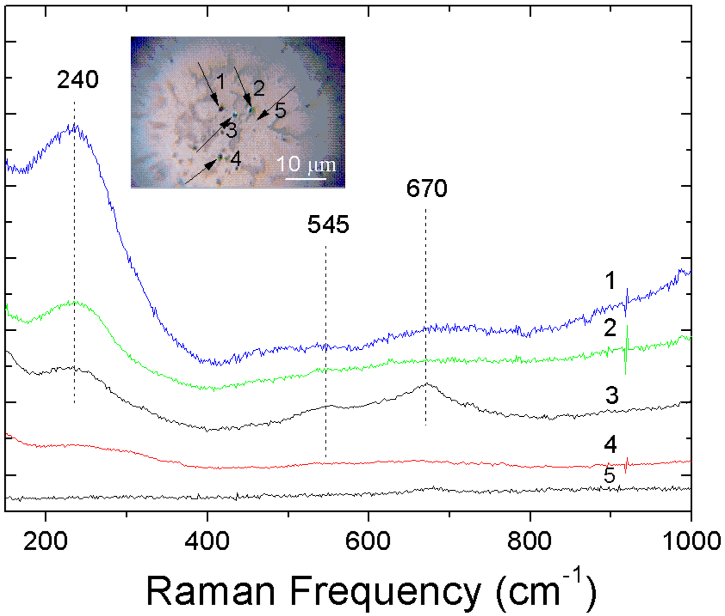
corrosion inhibition effect of the ILs through the adsorption on the metal surface and blocking active sites surrounding MnS inclusions

# Raman analysis-Detection of corrosion products

7% DEA, 6.9% MDEA




7% DEA, 6.9% MDEA and 7% ILs

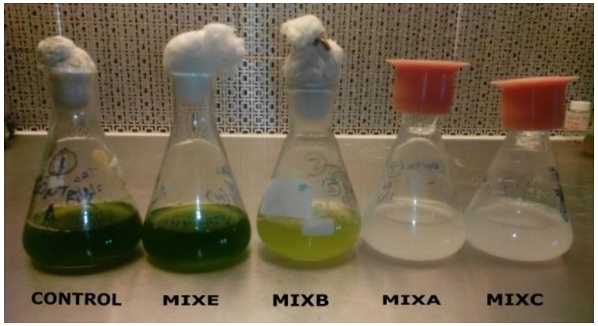


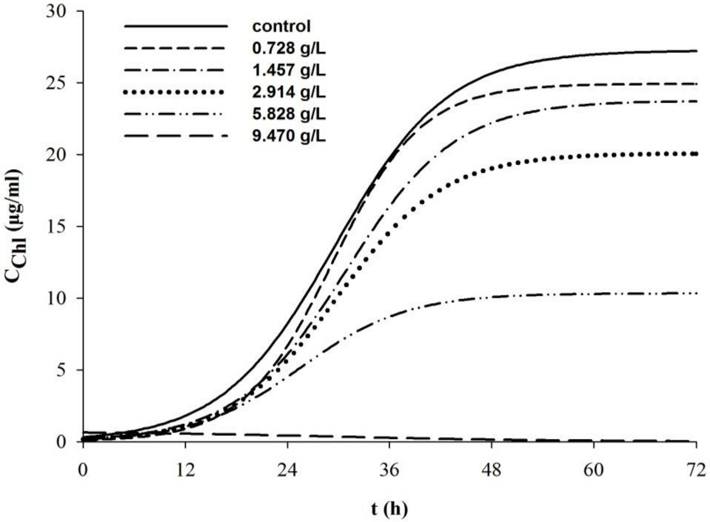

a-FeOOH (goethite)

# IOLICAP-Results

## Less Toxic

| | MDC (g/L) | MIC (g/L) | |
|---|---|---|---|
| **DEA** | 1.577 | 1.314 | 20% DEA |
| **MDEA** | 2.234 | 1.787 | |
| **MIXA** | 2.016 | 1.008 | |
| **MIXB** | 5.704 | 4.278 | 7% DEA, 6.9% MDEA and 7% ILs |
| **MIXC** | 2.809 | 0.175 | |
| **MIXE** | 9.470 | 4.371 | |



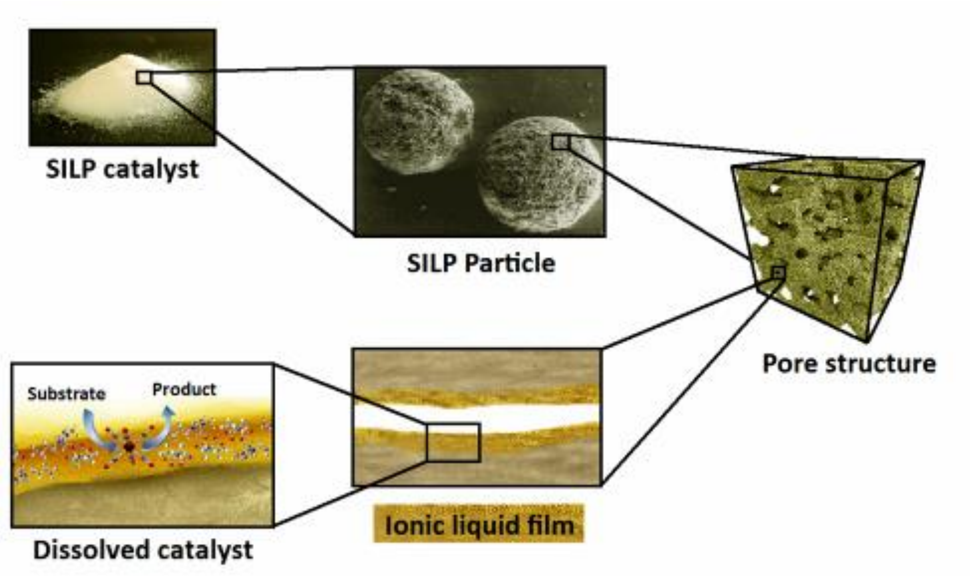



# As a way to confront the problems of

**High Viscosity** @ RT – 15-500cP $\Rightarrow$

**Binary $CO_2$/IL diffusivity** – $10^{-11}$ to $10^{-9}$ $m^2/sec$

**Cost** – 100-200€ at the 100kg level




- Confinement enhances $CO_2$-capture performance.
- Overcomes diffusion limitations- Very thin film.
- Cost- Less quantity of IL

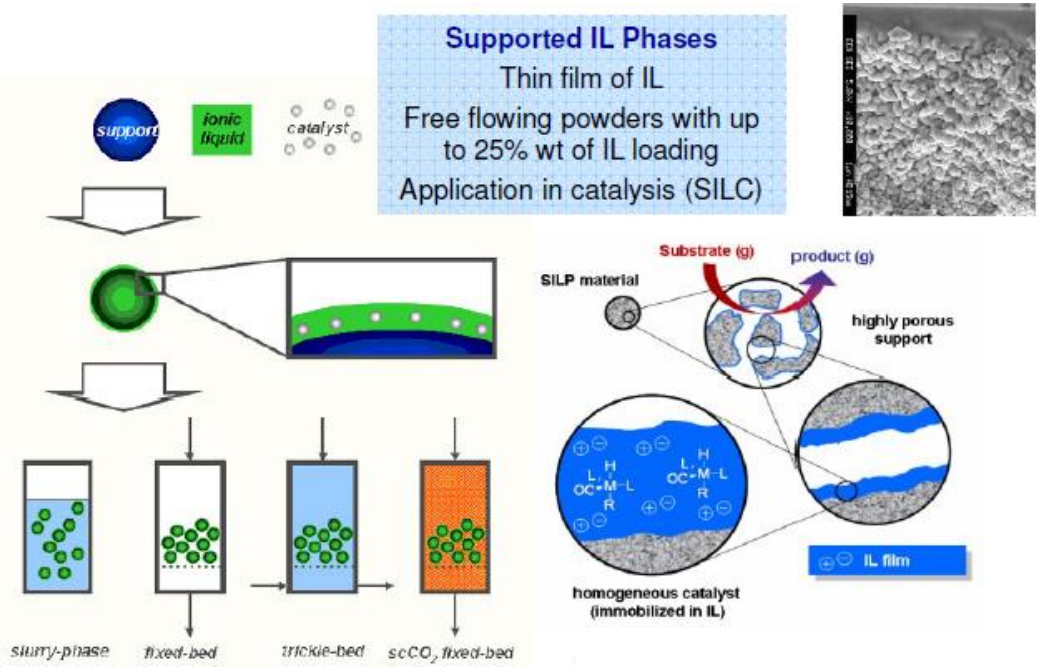
# The SILP concept

**Membranes = Supported Ionic Liquid Membranes (SILMs) – (70%)**

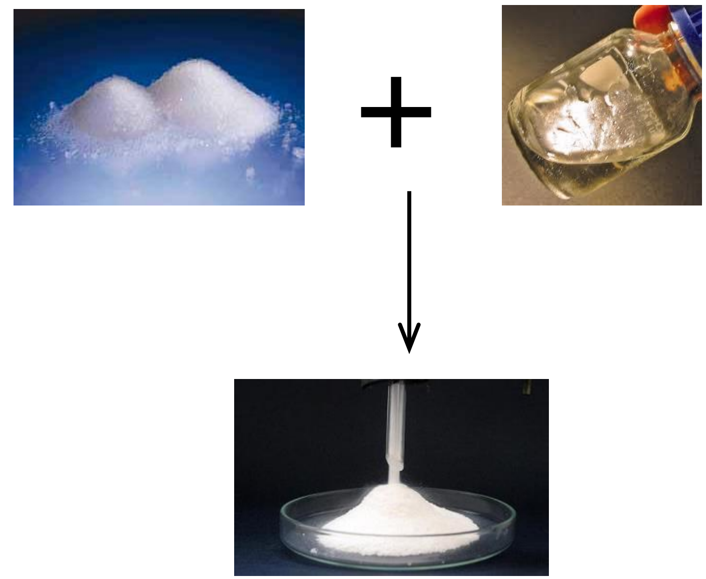
**Catalysts = Supported Ionic Liquid Catalysts (SILCs) – (25%)**

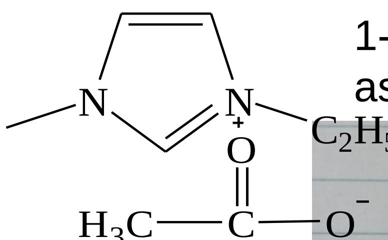
**Adsorbents = Supported Ionic Liquid Phase Adsorbents (SILPs) – (5%)**

# Ionogels-different from SILPs

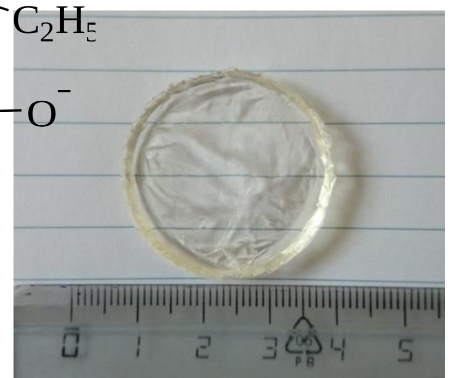


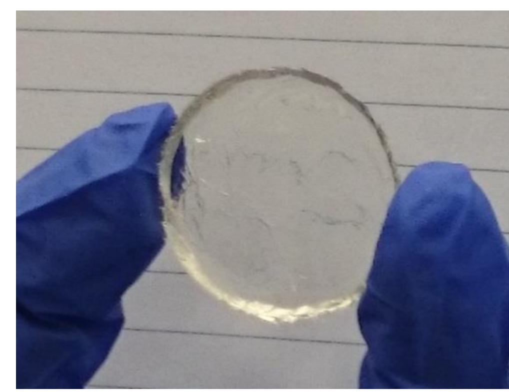

## SILPs





1-ethyl-3-methyl-imidazolium acetate [EMIM] [AC] as structure directing agent



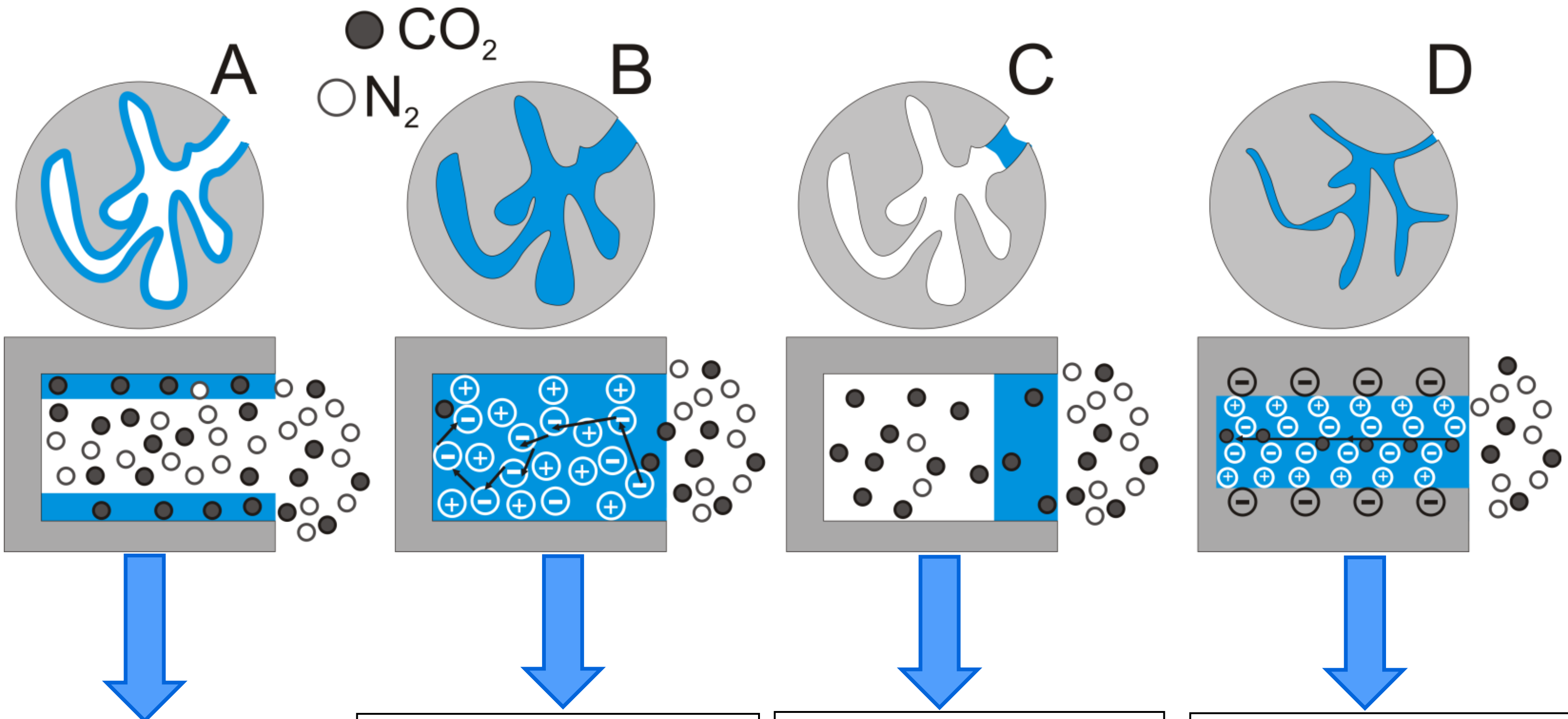


**Ionogels** Sol-gel.

Ionic liquids act as:

- drying control chemical additives
- catalysts
- structure directing agents
- solvents (or cosolvents)

# Using porous substrates and membranes



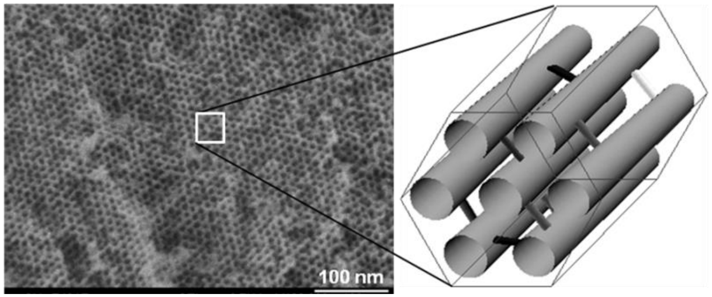

-Perfect for catalysis
-Gas separation? N

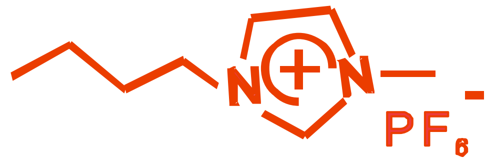
-Excellent gas separation
-Absorption capacity?
-Kinetics of absorption? Slow

-Excellent gas separation, fast kinetics
-Absorption capacity? High
-Stability and regeneration?

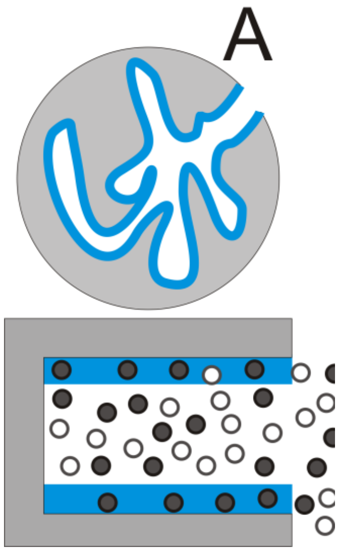
-Size of the pore comparable to the size of IL
-Orientation of the IL ions generate straight paths-fast diffusion

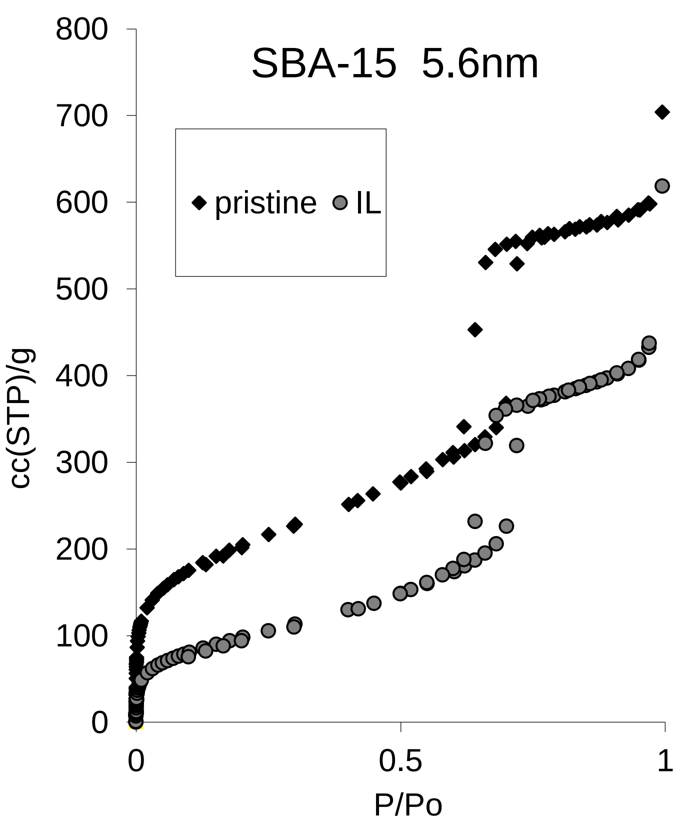
# Case A – Thin film on the pore walls

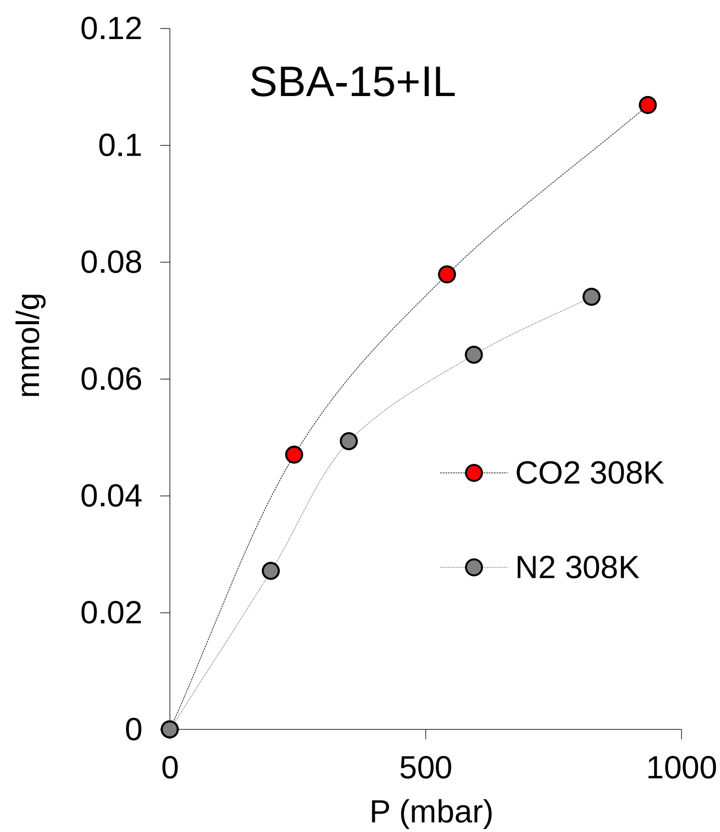


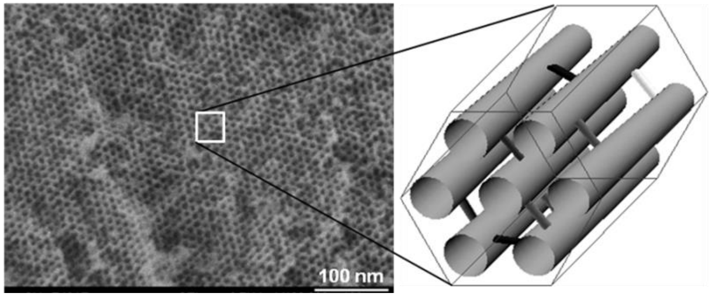

+ MeOH

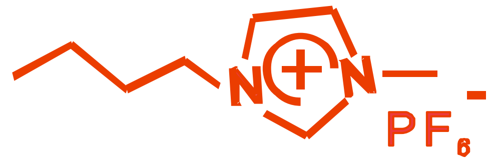


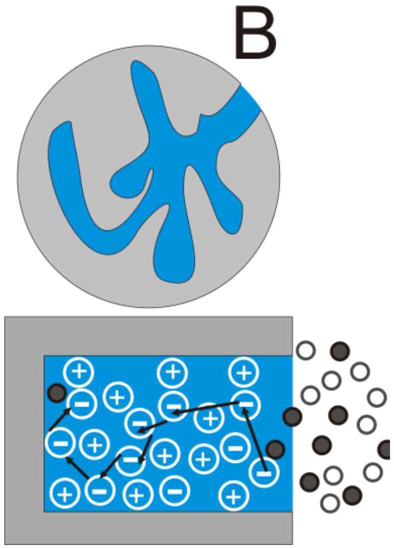



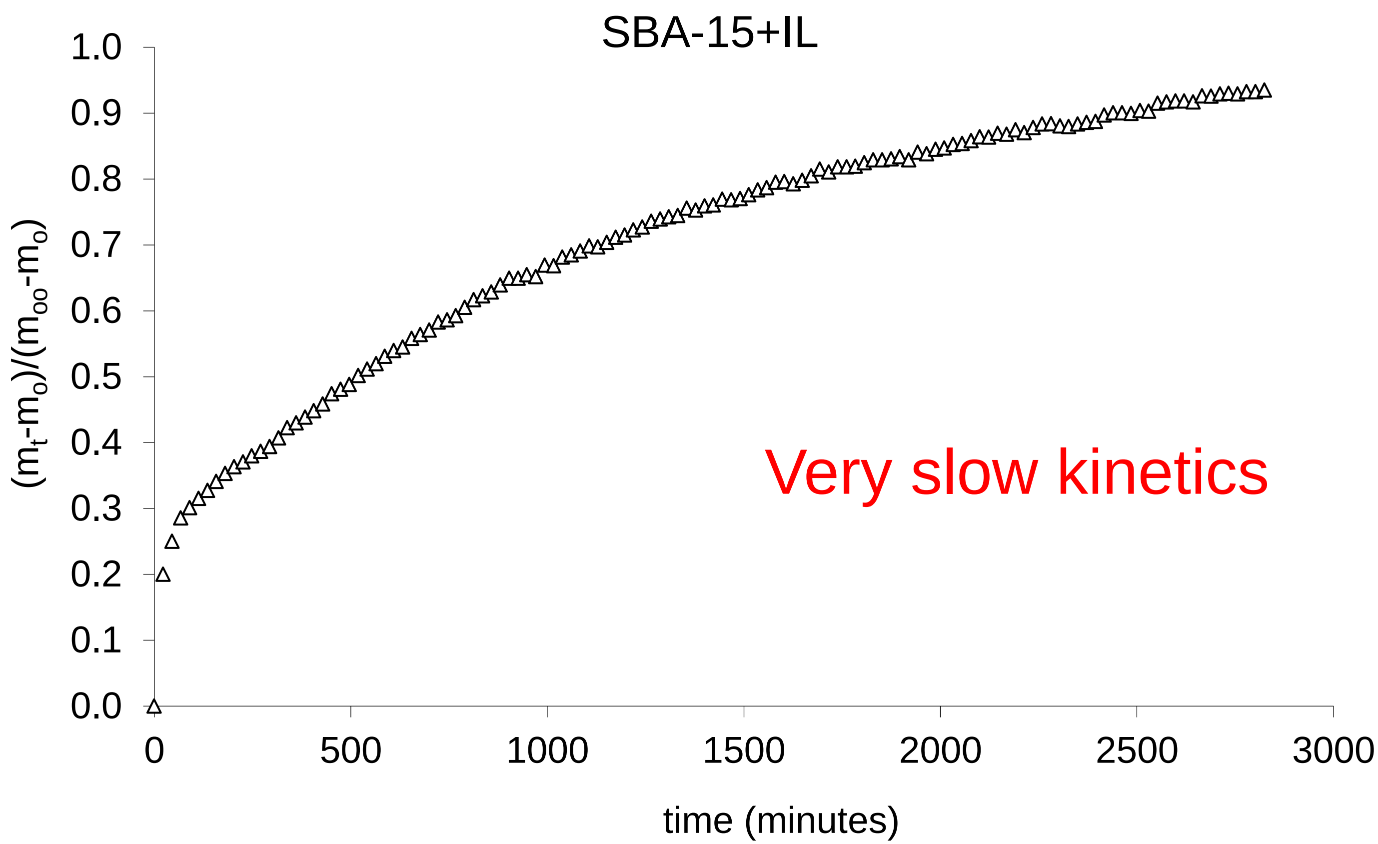



# Case B – Complete pore filling



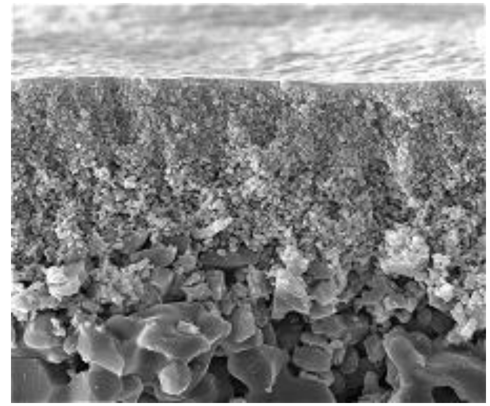



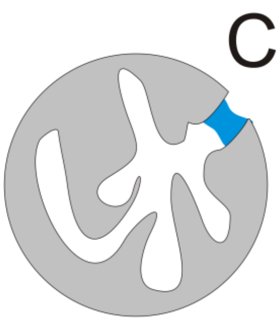



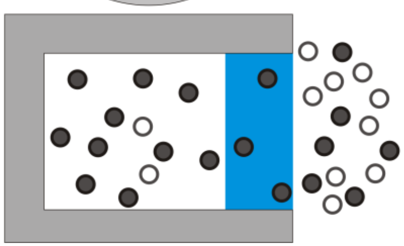



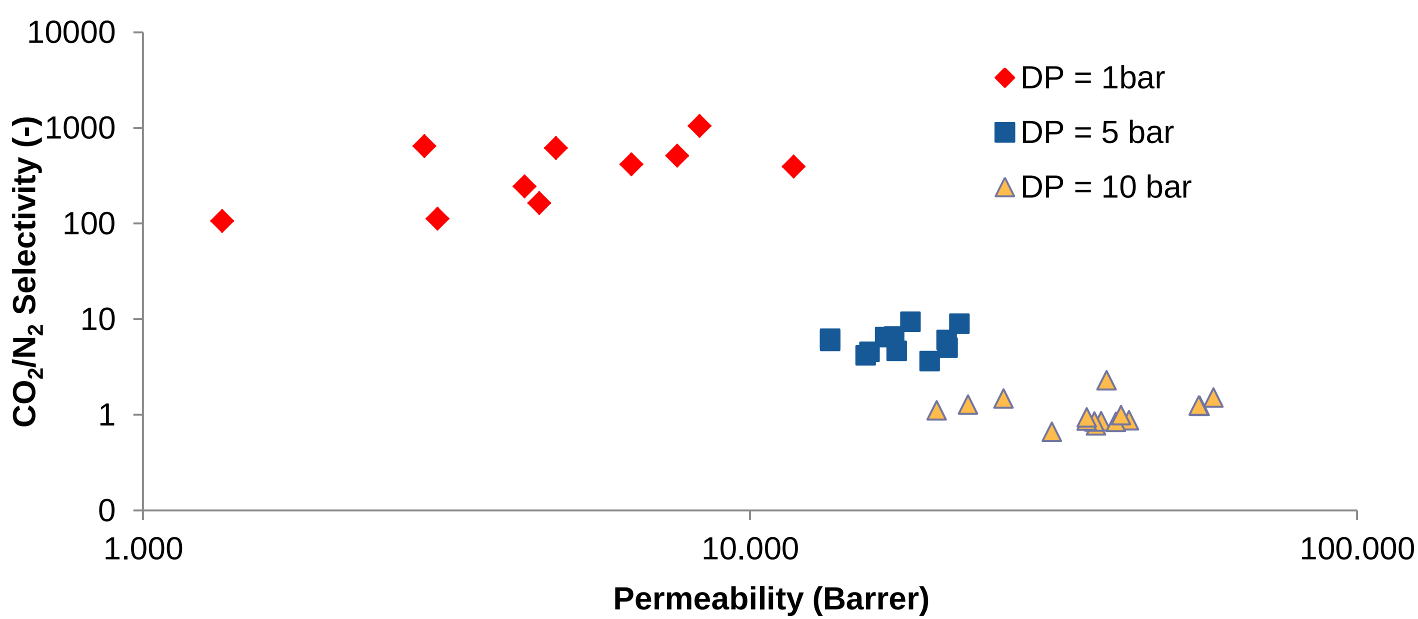
# Case C – Thin film on the pore mouth

## Ceramic Ultrafiltration and Nanofiltration membranes



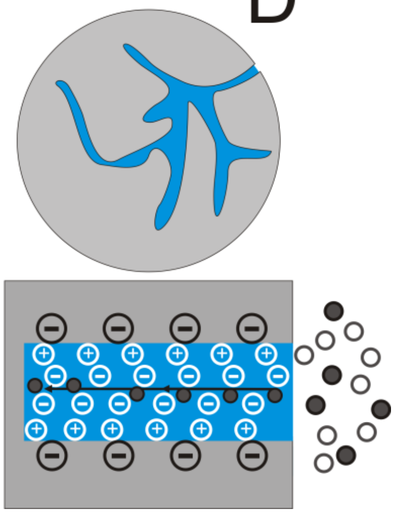




# Case D – Orientation of the IL ions

D

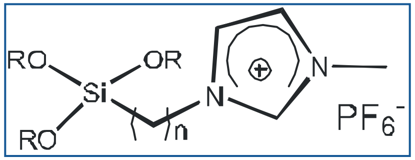


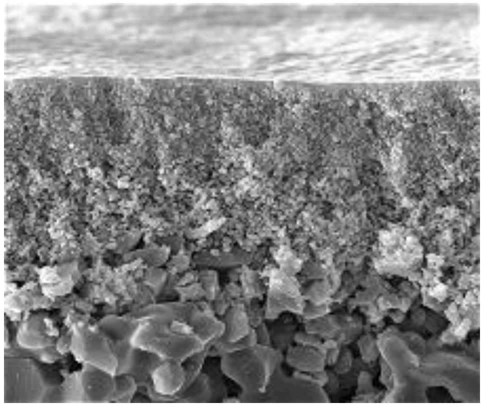
Challenges

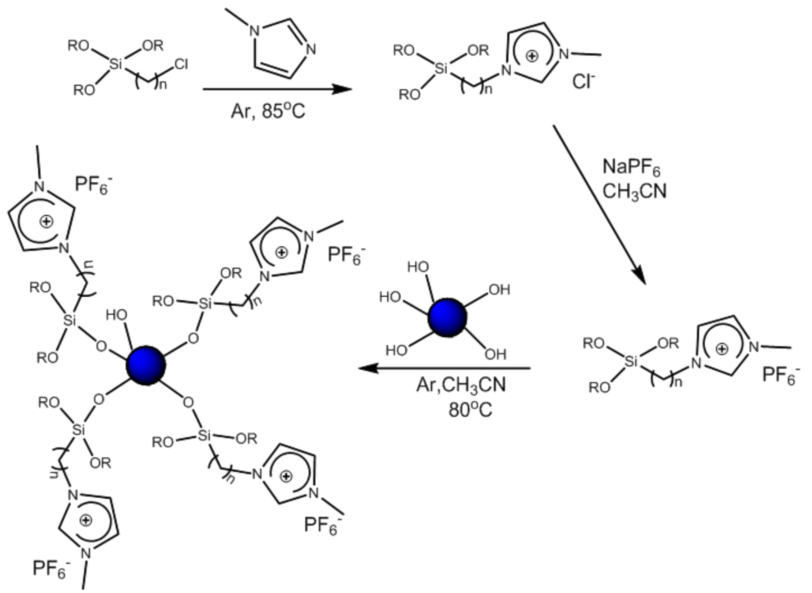
-It is difficult to find porous supports with the required pore size

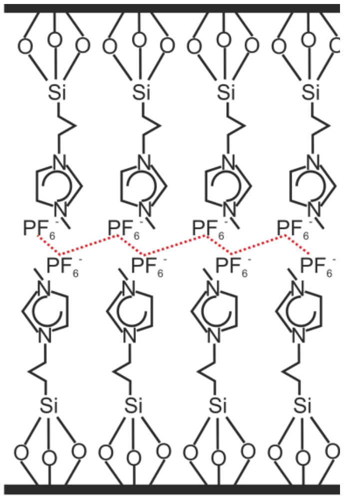
-The surface of the porous solid must be negatively charged

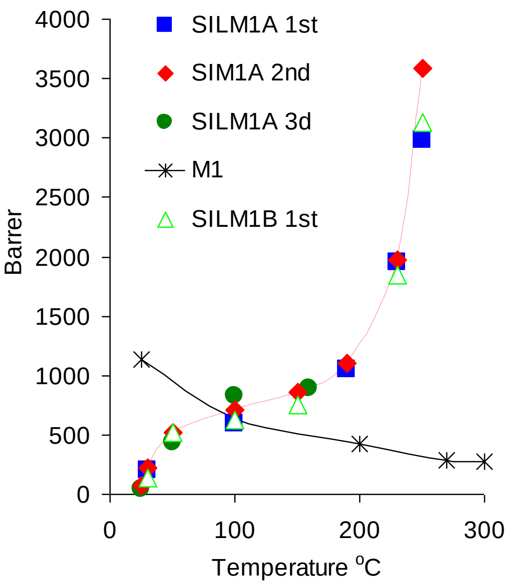
# Case D – Alternative method - Grafting

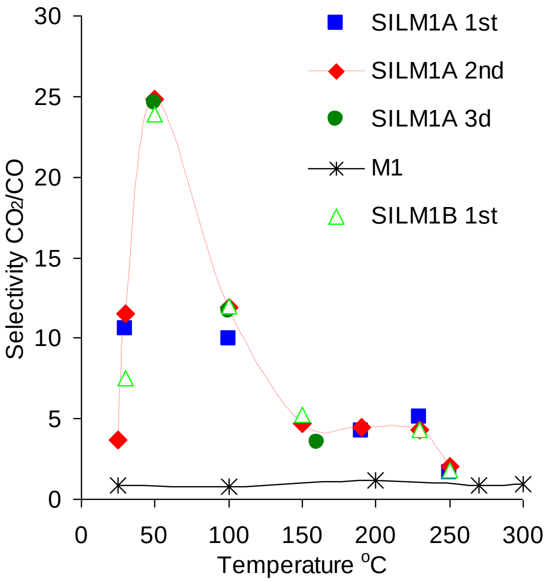


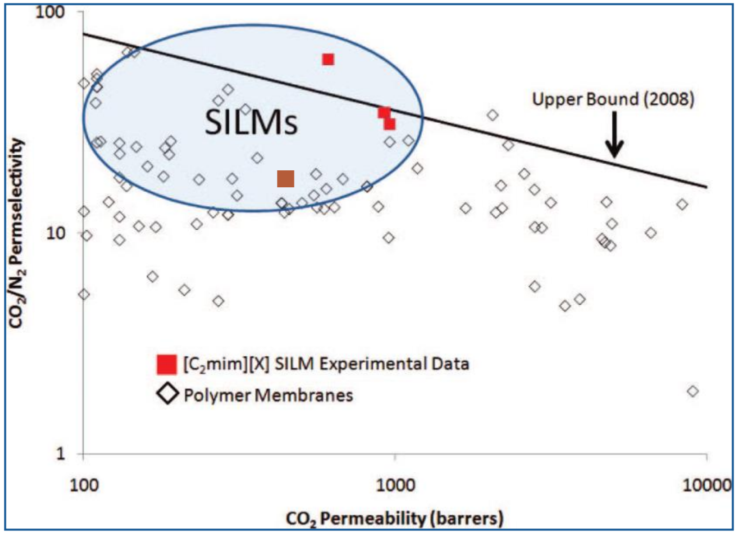





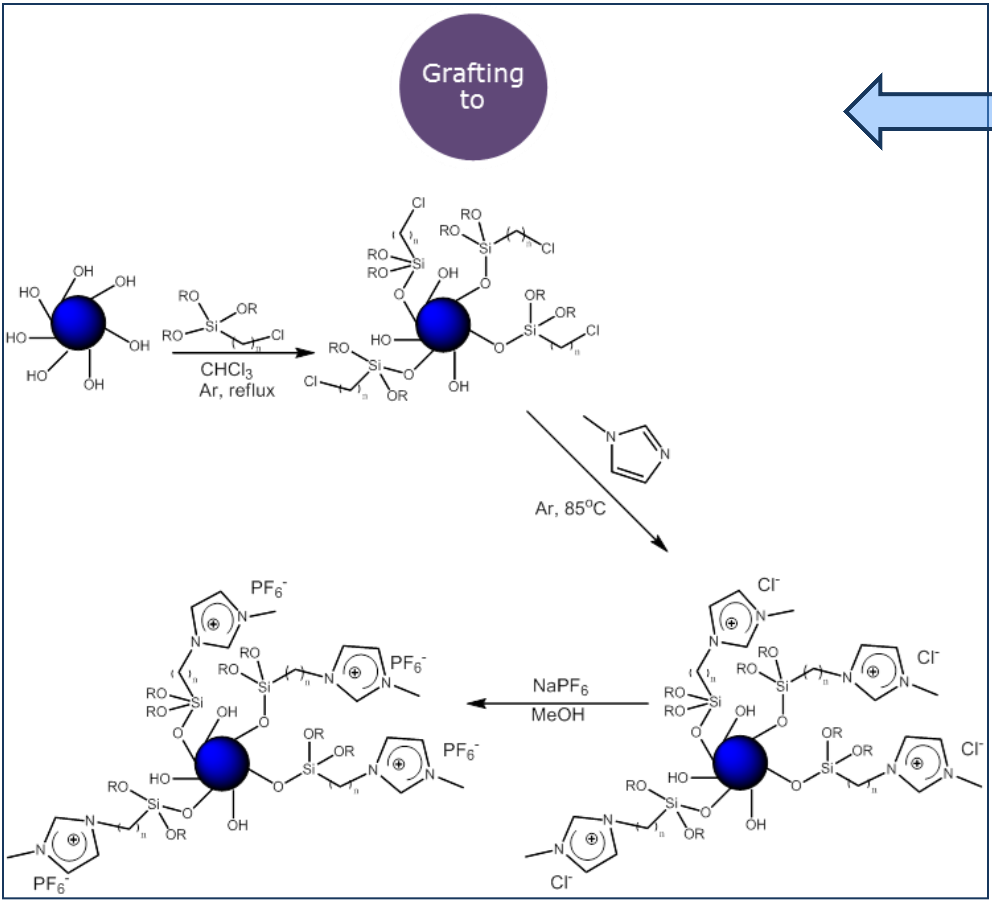



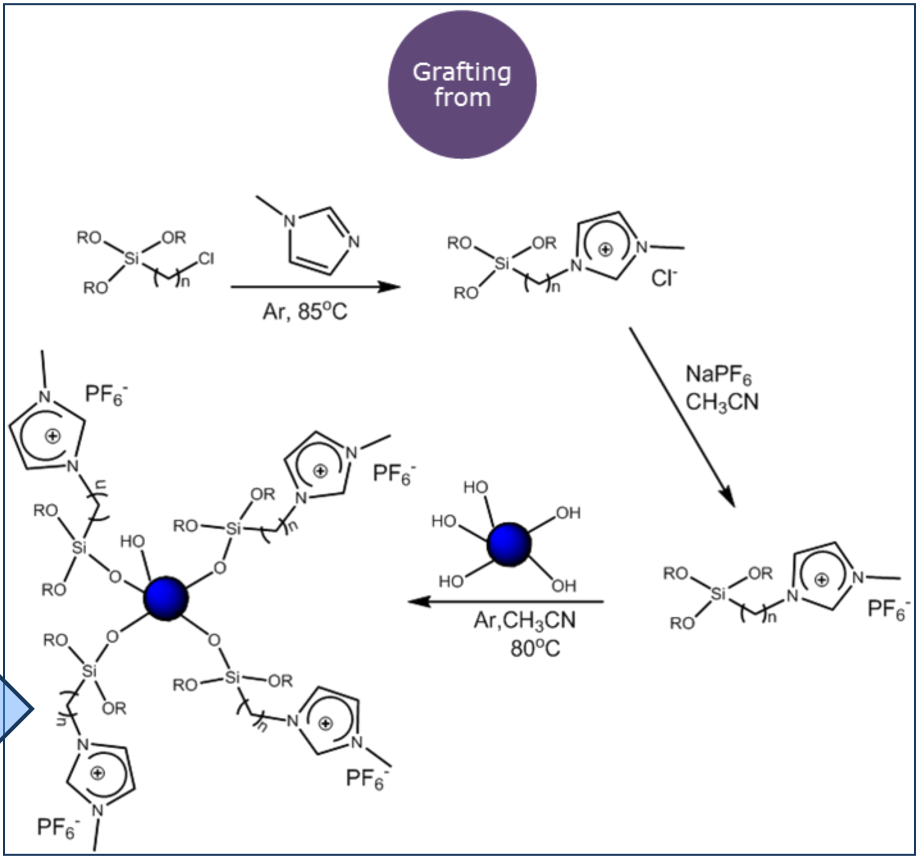



# Different approaches for development

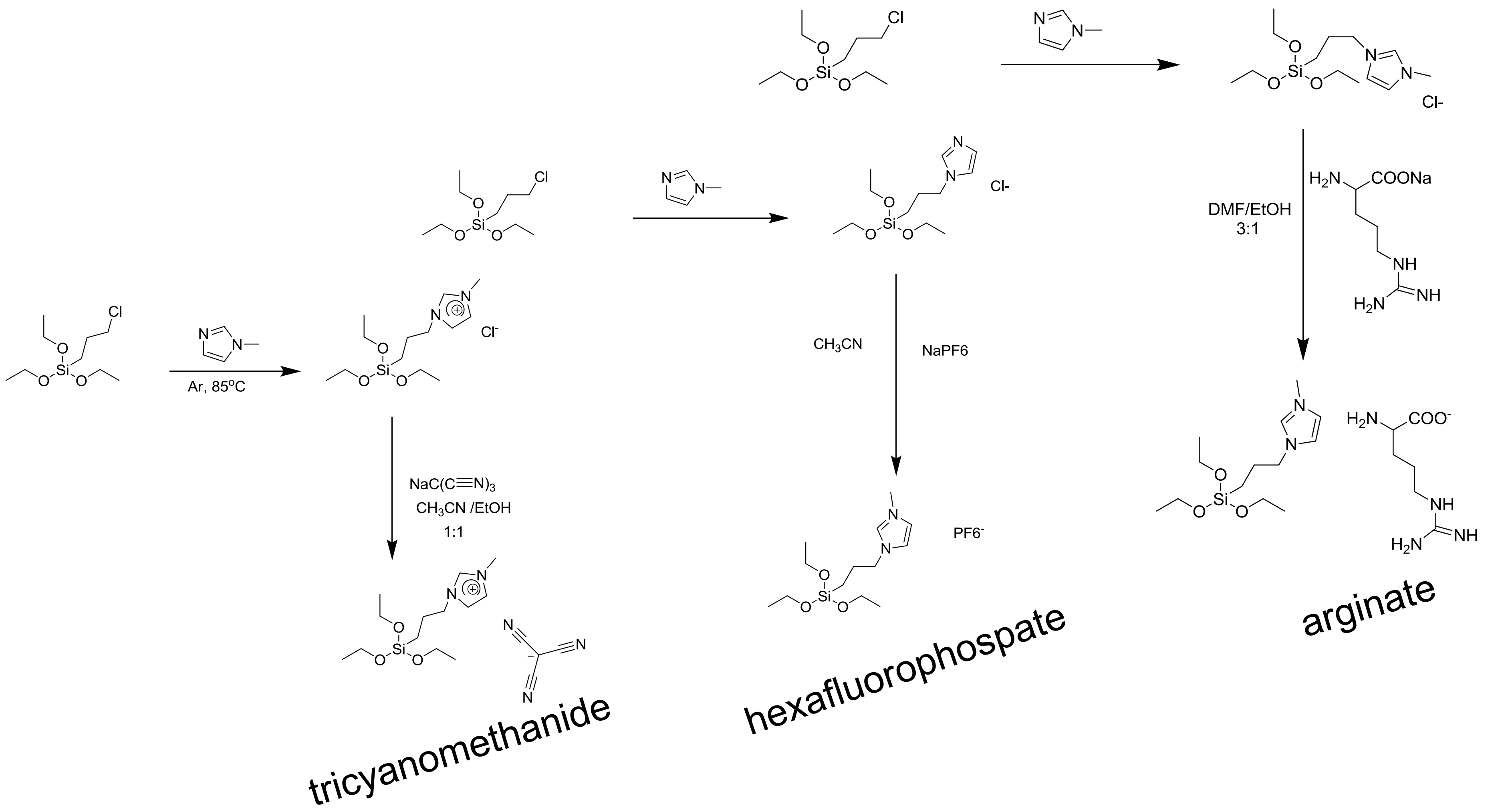



First step to graft the silane

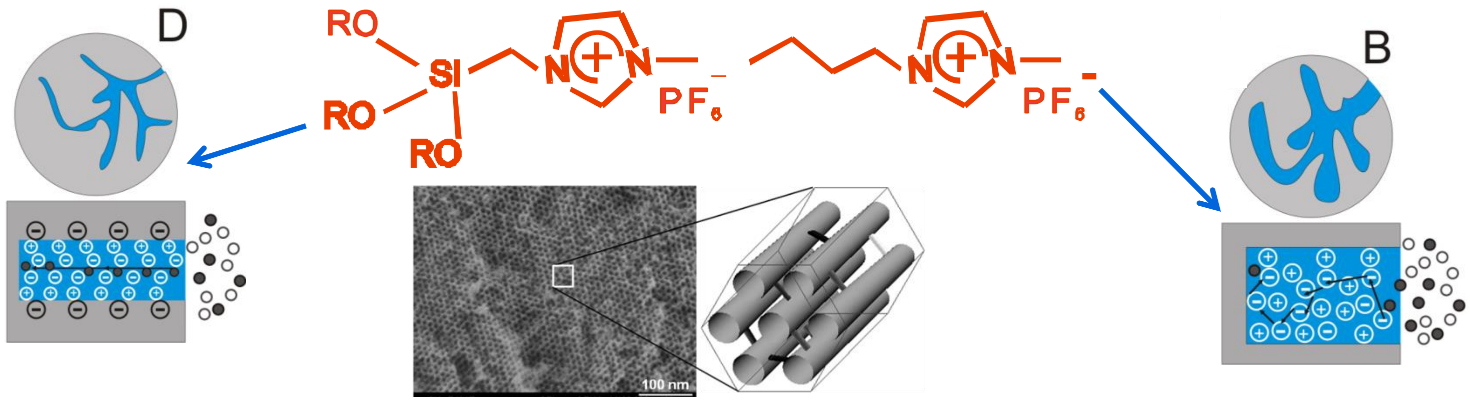


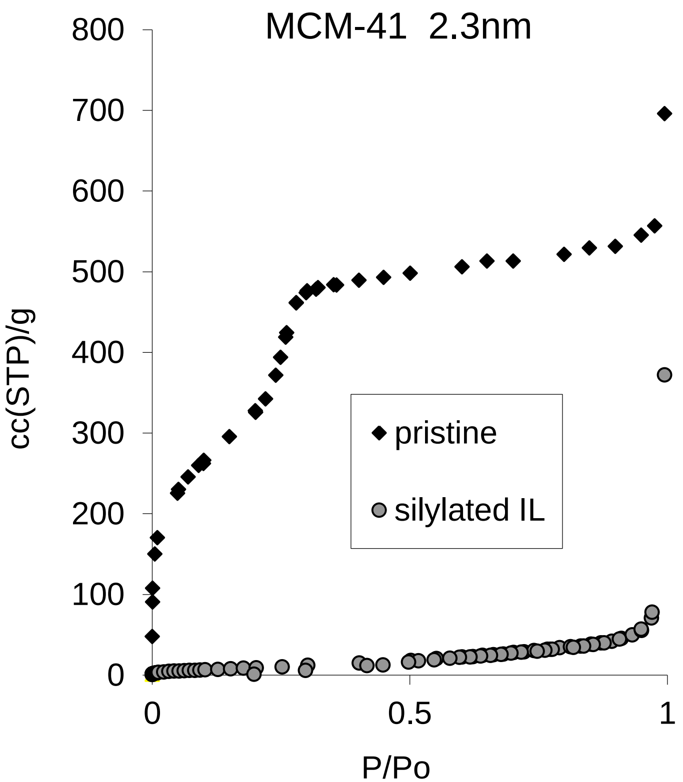

First step to synthesise the silylated IL
and graft it to the pore surface

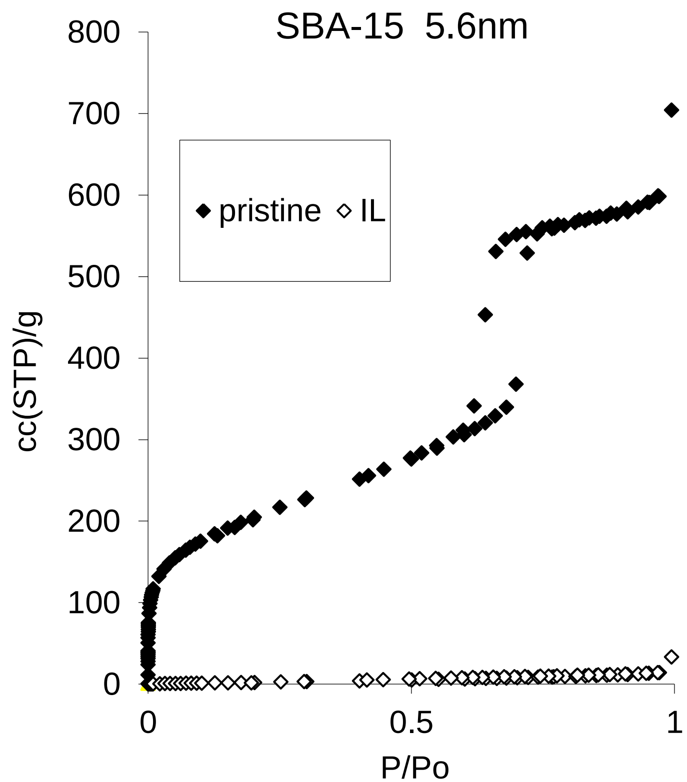
# Very versatile technique-Different anions



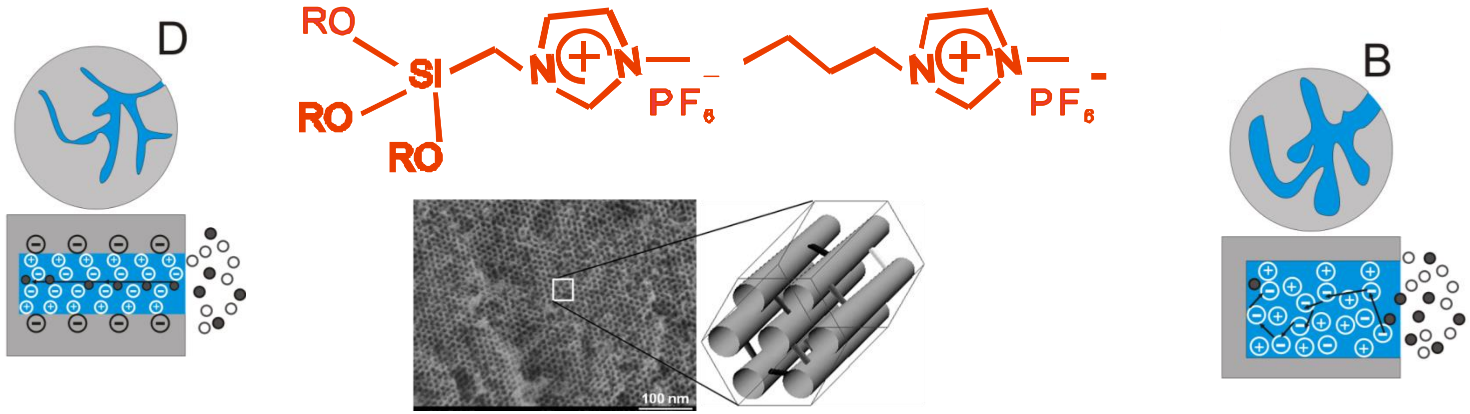
# Comparison Grafted vs Case B

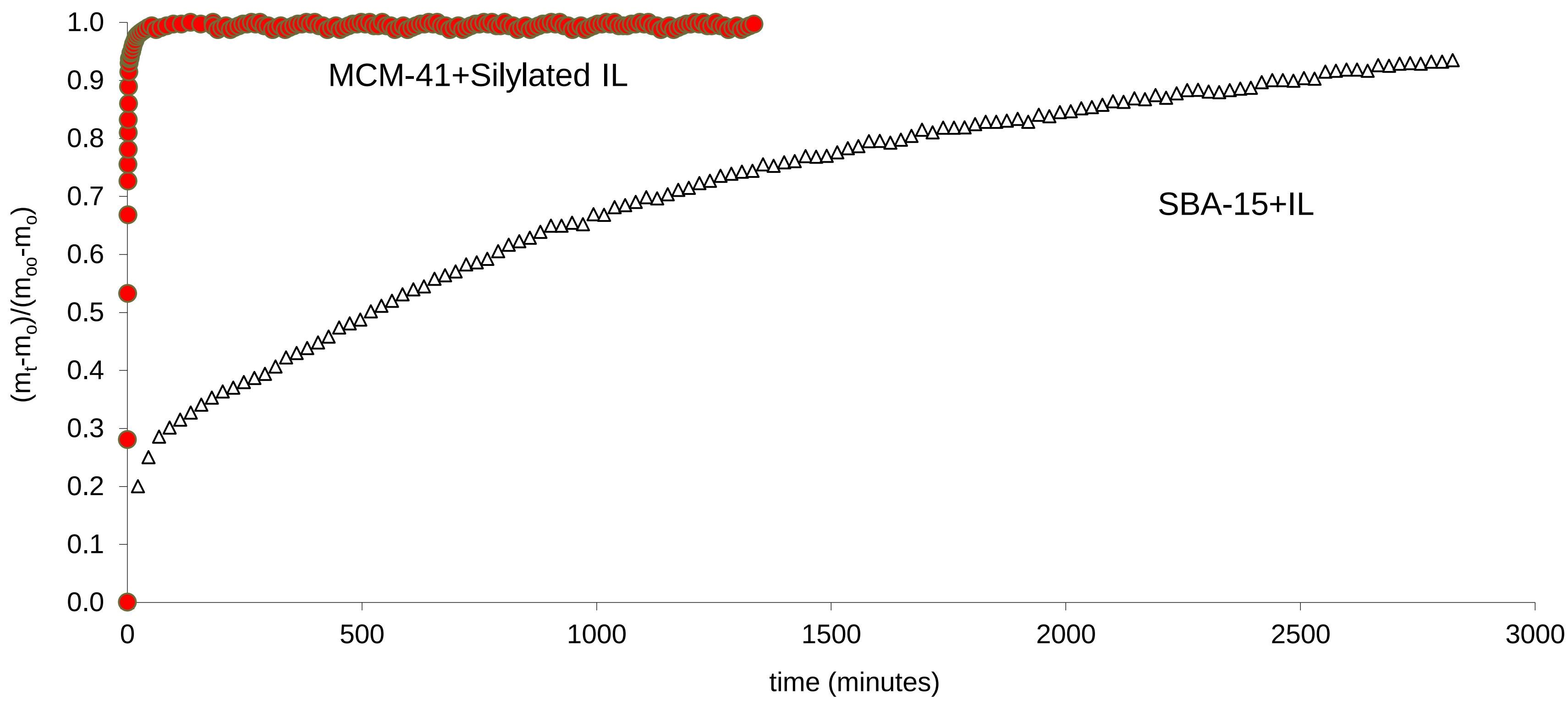


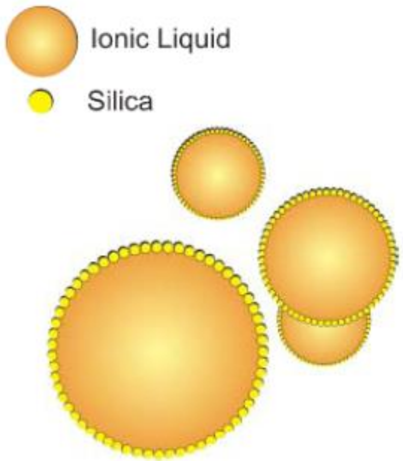
# Comparison Grafted vs Case B



# Novel SILPs– Inverse SILPs

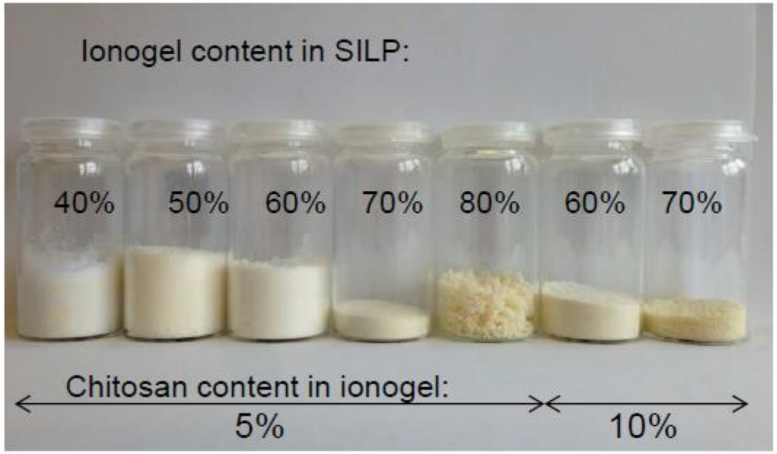
Innovation - Dry liquid. Tiny droplets of IL (<1μm) covered by nanoparticles of pyrogenic silica

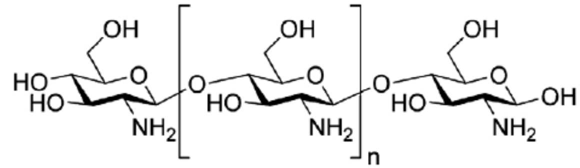



- ✓ Easily upscalable development
- ✓ Phase inversion from silica nanoparticles suspension in a methanolic solution of the Ionic Liquid.
- ✓ By controllable evaporation of methanol we achieve phase inversion with the hydrophilic nanoparticles covering the droplets of IL.

# Morphology of Inverse SILPs

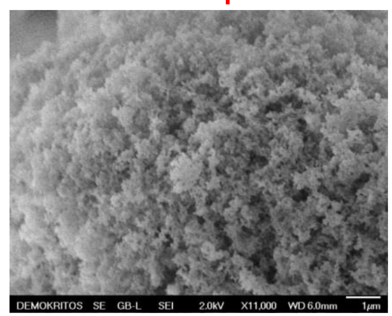
Novelty- Use an Ionogel of Chitosan with the IL



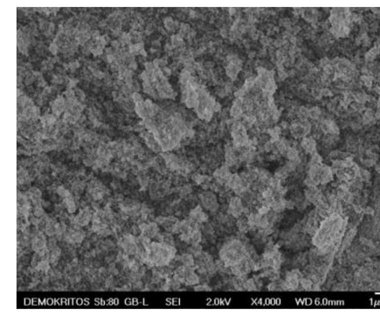




## Images from SEM

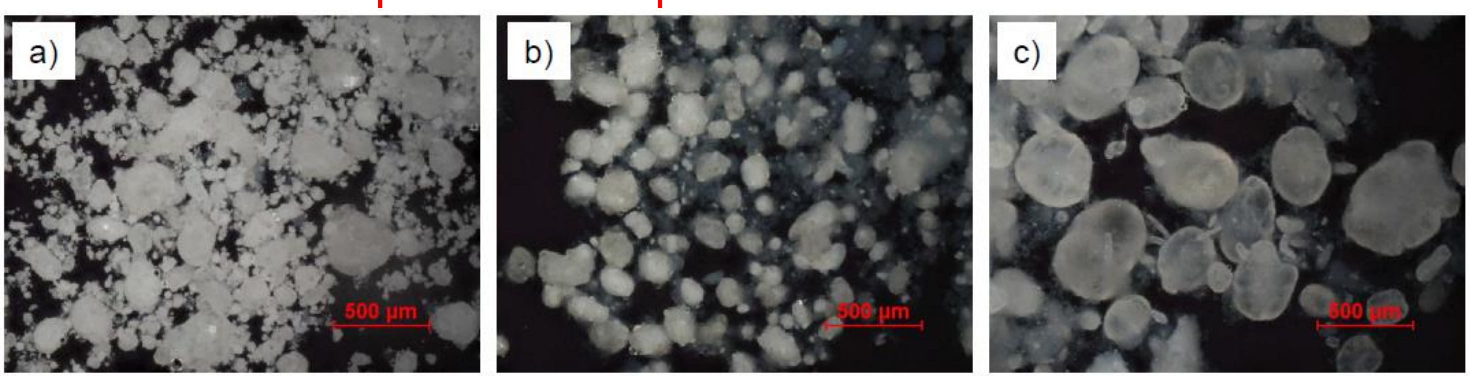
Silica nanoparticles



Inverse SILP

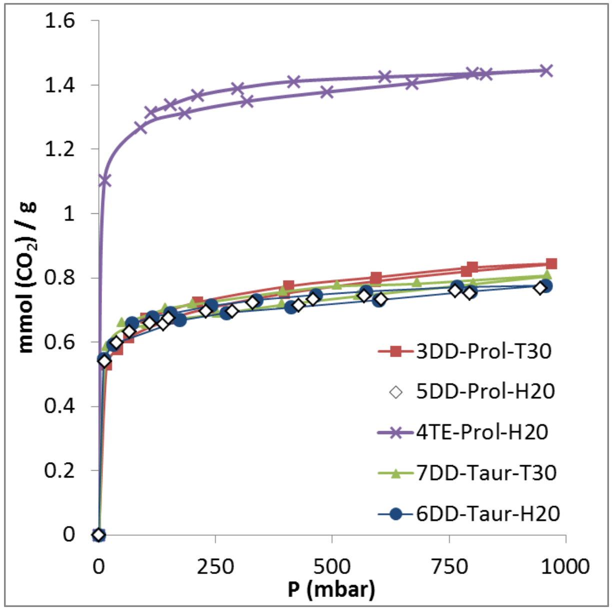


Optic Microscope

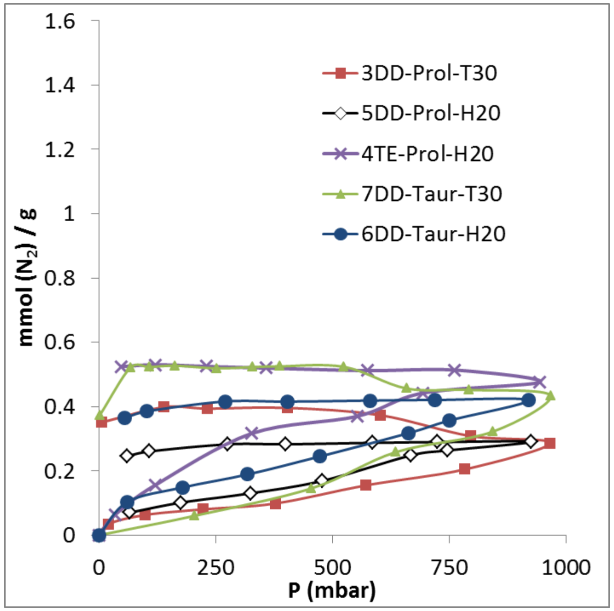


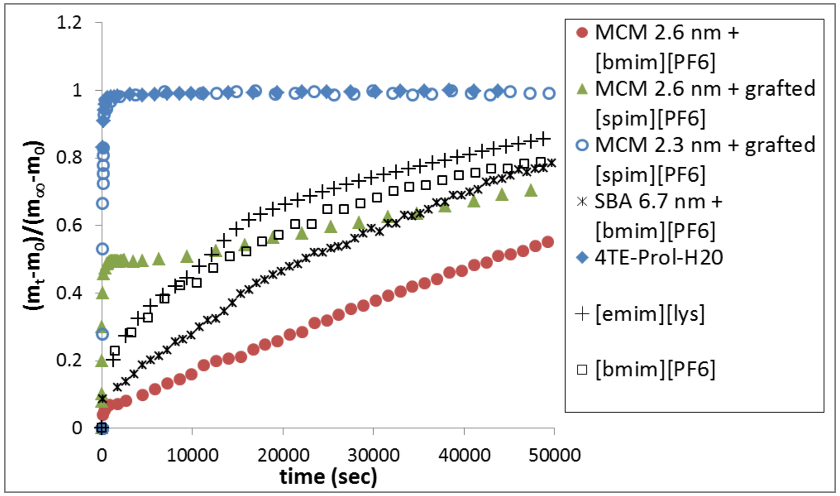
# Performance of Inverse SILPs

$CO_2$




$N_2$




Very fast kinetics

Characteristic numbers for Ionic Liquids

| | |
|---|---|
| # of predicted permutations of ions | $10^{18}$ |
| # of liquid materials | $10^{12}$ (?) |
| # of materials with interesting properties: | ~ 10.000 |
| # produced by companies on lab scale today: | ~ 500 |
| # procuded on lab scale in future: | ~ 1500 |
| # of materials produced on industrial scale today | 5-10 |
| # produced on industrial scale in future: | 25 (?) |
| # of materials described in literature today | > 2000 |
| # of materials synthesized in our own labs | > 700 |
| **# of suifficiently characterized materials** | **~ 20** |

# Ionic Liquids in gas separation

CHEMICAL REVIEWS

Review

pubs.acs.org/CR

## Gas Solubility in Ionic Liquids

Zhigang Lei, Chengna Dai, and Biaohua Chen*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Box 266, Beijing, 100029, China

dx.doi.org/10.1021/cr300497a1 *Chem. Rev.* 2014, 114, 1289

$CO_2$ - 120 ILs

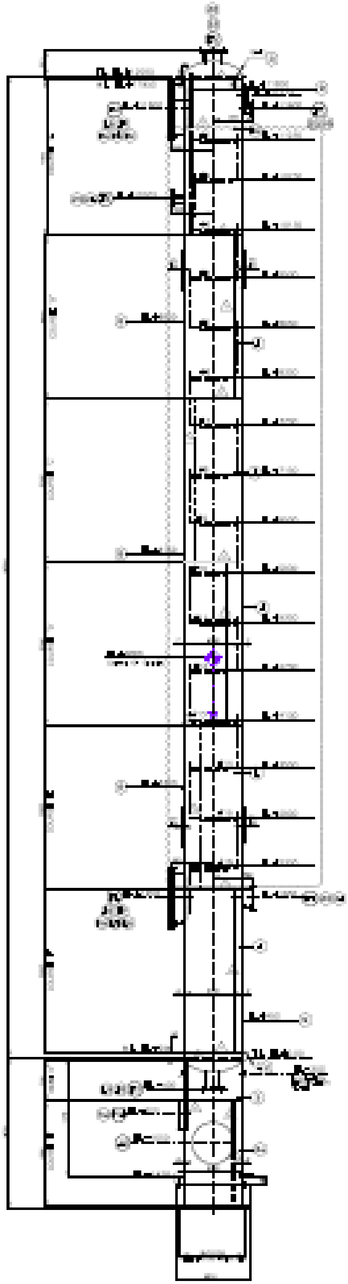
$N_2$ -10 ILs

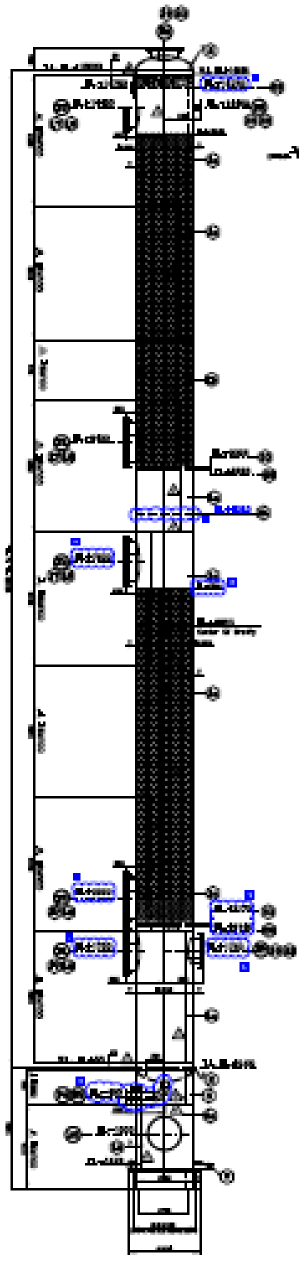
$SO_2$- 20 ILs

$H_2S$ - 16 ILs

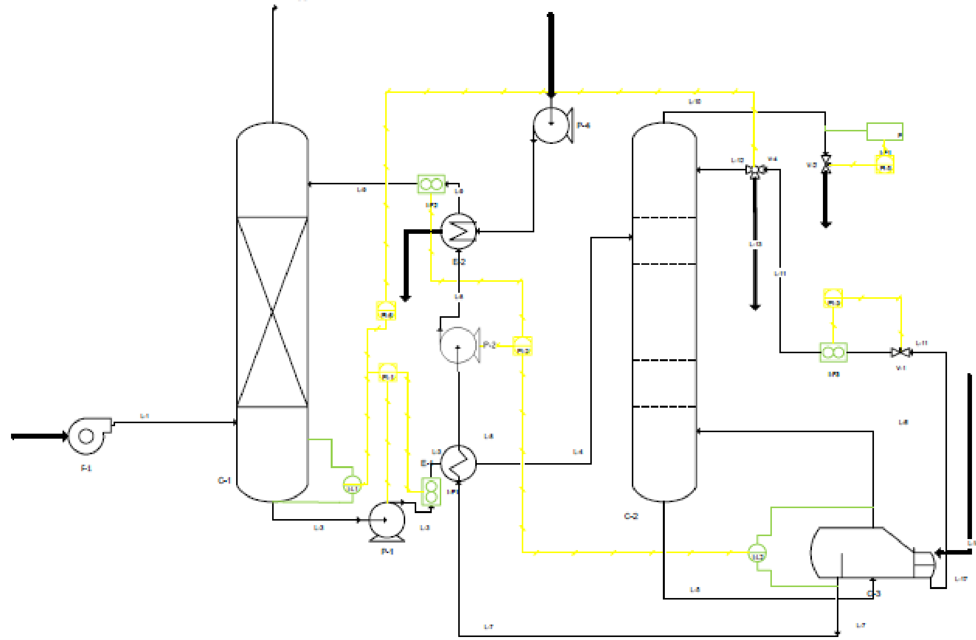
$N_2O$ – 11 ILs

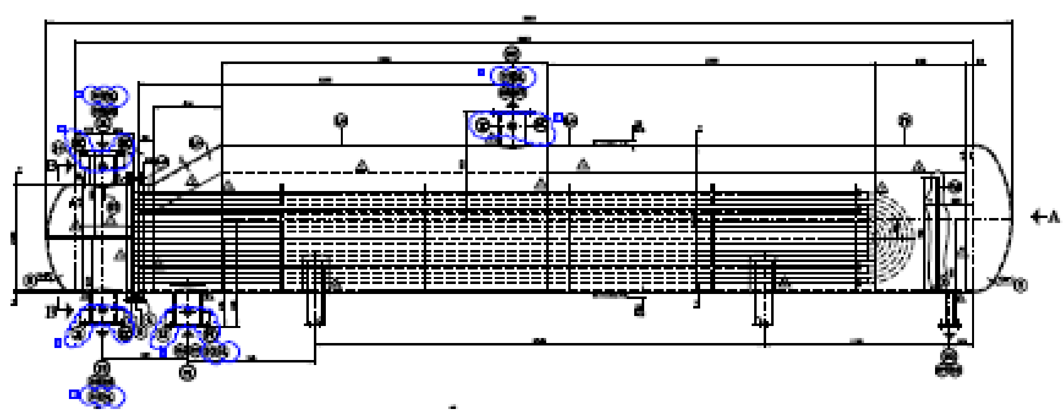
# Ionic Liquids in gas separation





## Demonstration: Budget 350k€
## 5000Nm$^3$/h





## Flue Gas desulfurisation Plant

# Power Plant



# Power Plant



# Thank you for your attention !!!!

# IOLICAP-Results