

*Leuven Ionic liquid Summer School*

**23. – 27. August 2010**

# **Ionic Liquids at BASF SE**



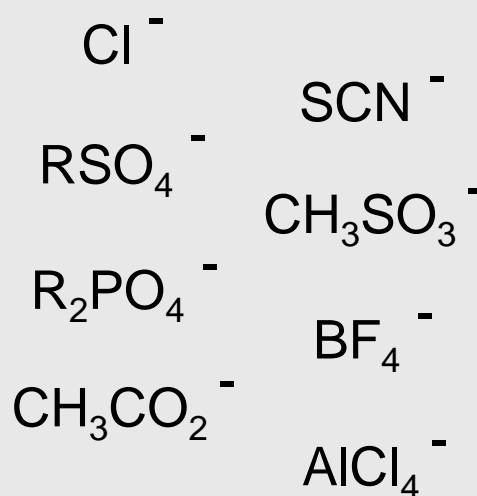
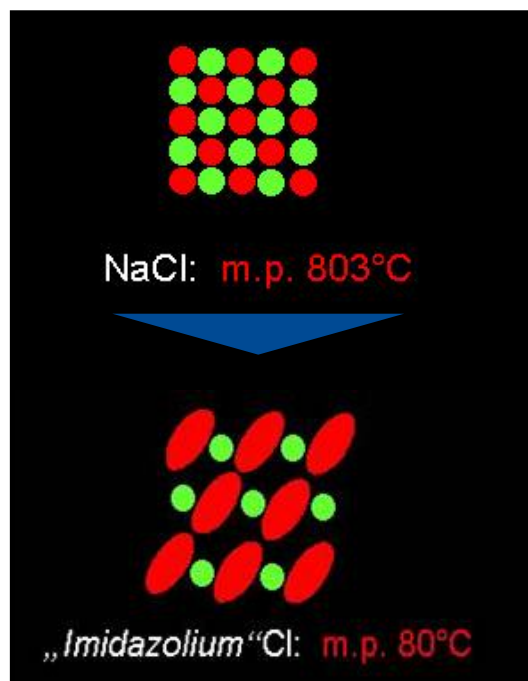
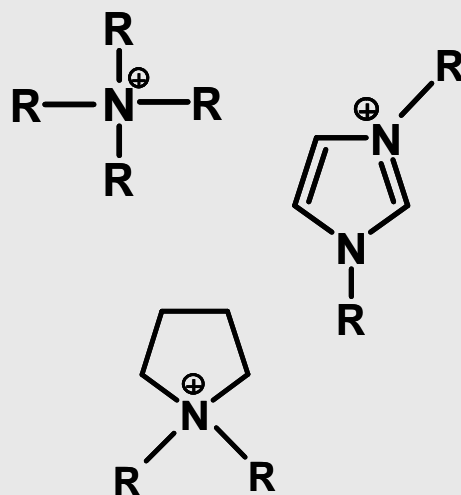
The Chemical Company

**Dr. Klemens Massonne**

BASF SE, Ludwigshafen

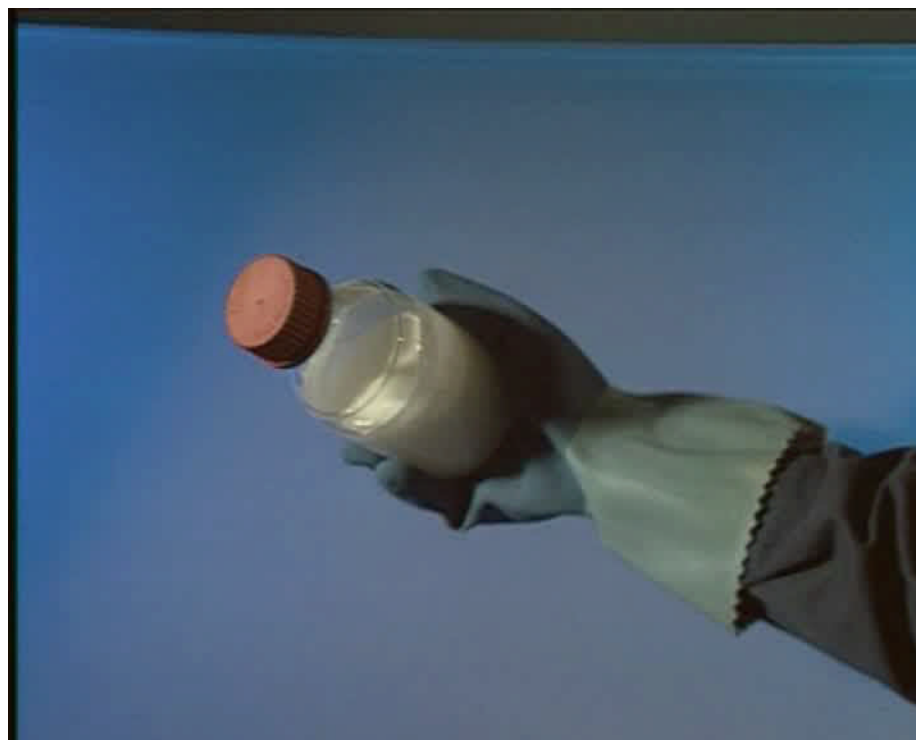
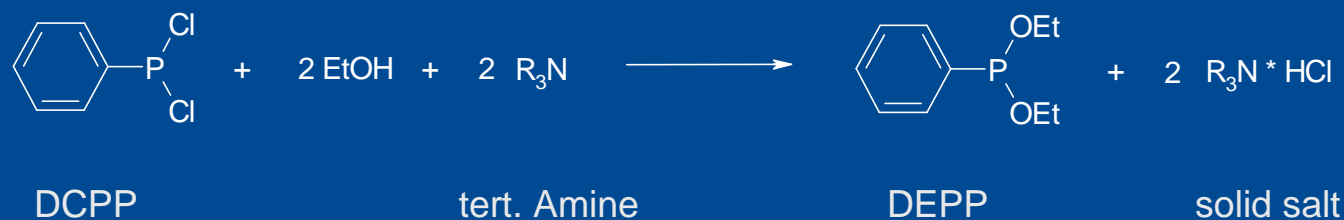
## What are Ionic Liquids ?

liquid salts  
m.p. < 100°C  
(often: < r.t.)



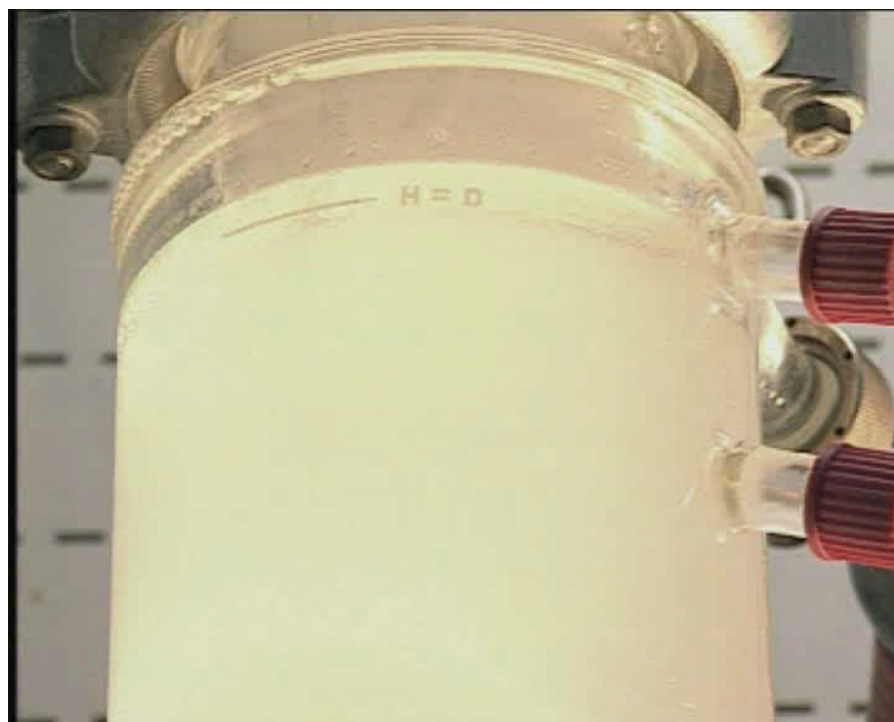
- literally no vapour pressure
- non flammable
- high therm. & mechan. stability
- broad liquid range
- electric conductivity
- high electrochem. stability
- exceptional diss. properties

## Solution of a Problem with IL: BASIL™

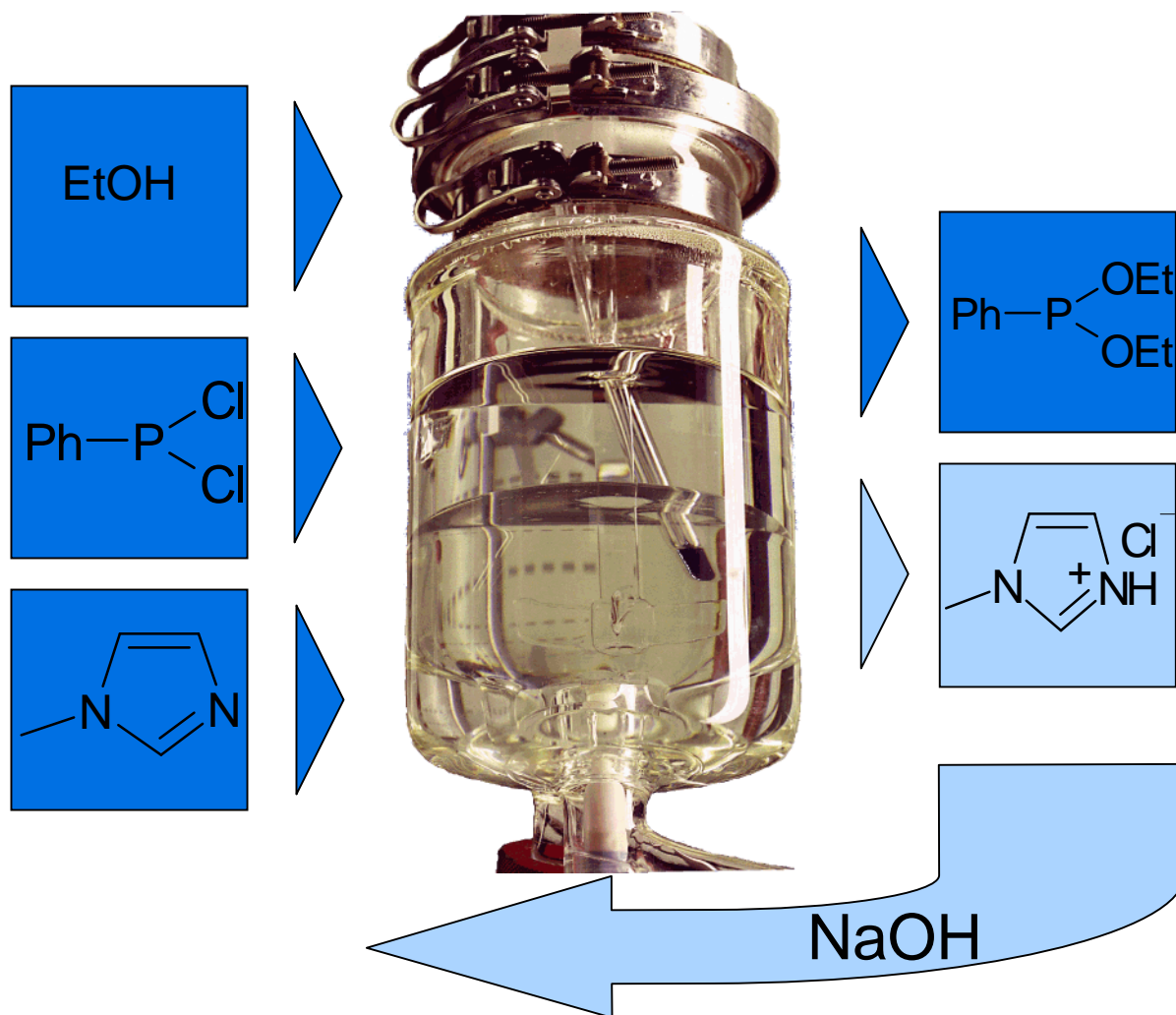


### Solution of a Problem with IL: BASIL™

### Acid Scavenging with Ionic Liquids: BASIL™

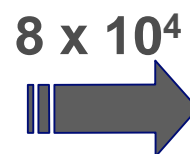


## Solution of a Problem with IL: BASIL™



## Solution of a Problem with IL: BASIL™

old process (with solids):  
yield per volume and time unit  
 $8 \text{ kg m}^{-3} \text{ h}^{-1}$



yield per volume  
and time unit  
 **$690.000 \text{ kg m}^{-3} \text{ h}^{-1}$**





## Ionic Liquids at BASF SE

### Solution of a Problem with IL: BASIL<sup>TM</sup>



**$8 \text{ kg m}^{-3} \text{ h}^{-1}$**   
**50 % yield**  
**waste**



**$10^5 \text{ kg m}^{-3} \text{ h}^{-1}$**   
**98 % yield**  
**recycling**

## How to get to the IL you really need ?

each IL represents an unique set of properties

### performance parameters

e.g. dissolution properties  
miscibility / immiscibility  
electric conductivity  
heat capacity

### physical properties

e.g. melting point / liquid range  
thermal stability  
corrosivity & compatibility  
viscosity

### product safety

e.g. LD 50 (oral / dermal)  
biodegradability  
ecotoxicology  
inflammation point

### chemical composition

e.g. cation / anion  
pH (in water)  
impurities  
(water, organic volatiles,  
halides, coloured impurities)



## Broad Range of Application Segments



### Chemical Processing

- e.g. reaction media in
- catalytic reactions
  - nucleoph. substitution
  - acid scavenging

### Metal Processing

- e.g.
- electroplating Al
  - electroplating Cr
  - electropolishing



### Separation Processes

- e.g.
- extractive distillation
  - extraction of aromatics
  - lignin / cellulose



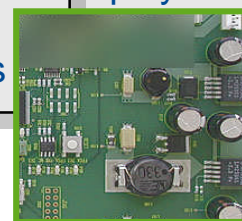
### Eng.& Functional Fluids

- e.g.
- Lubricants
  - Hydraulic Liquids
  - Absorption Cooling



### Electronic Devices

- e.g.
- Lithium Ion Batterie
  - Super Capacitors
  - Dye Sensitized Cells



### Polymer Processing

- e.g.
- regenerated cellulose
  - cellulose derivatives
  - polymer blends



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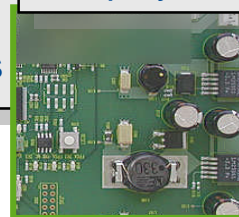
### Electrolytes

- e.g.
- Lithium Ion Batterie
  - Super Capacitors
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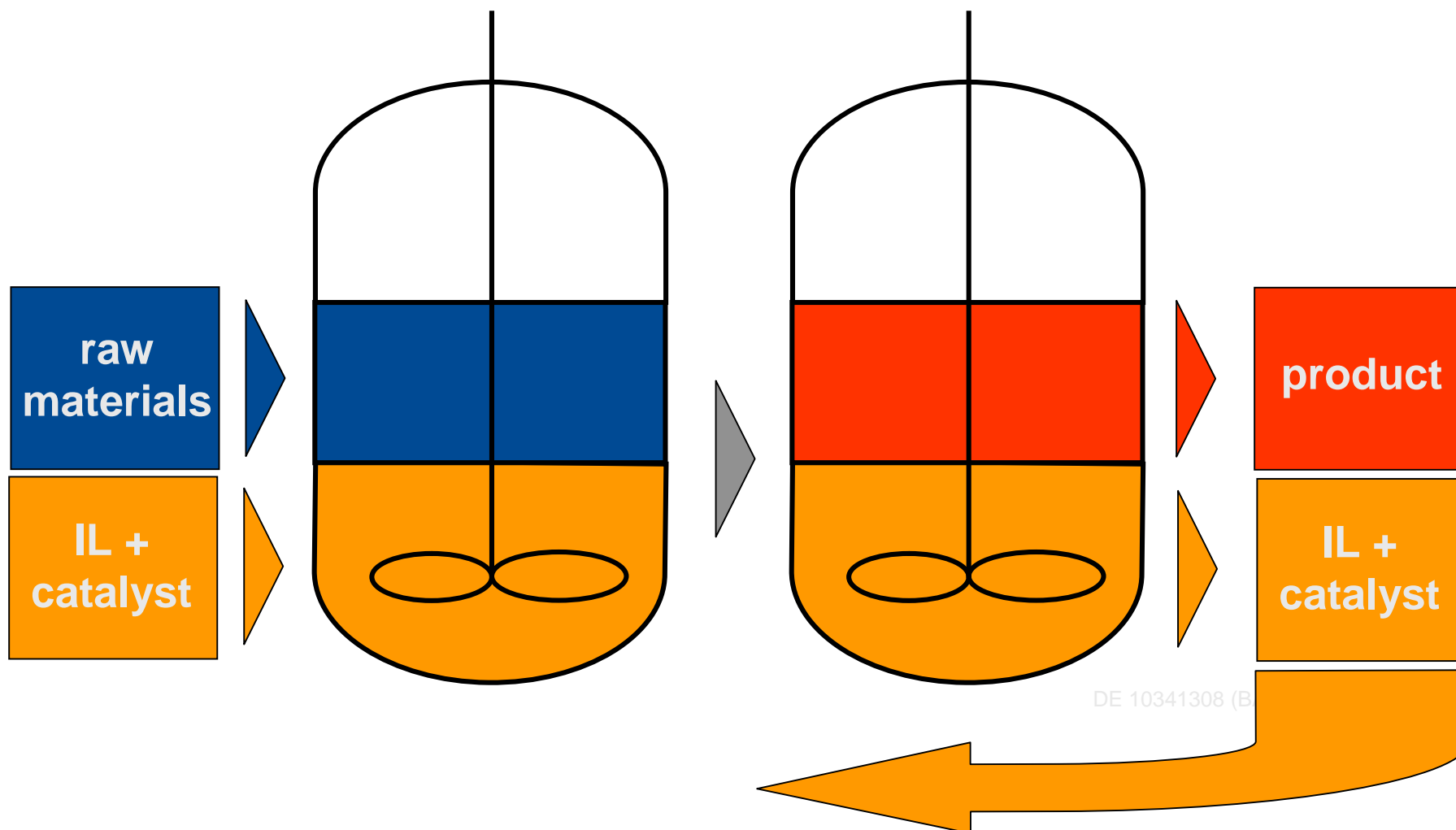


### Polymer Processing

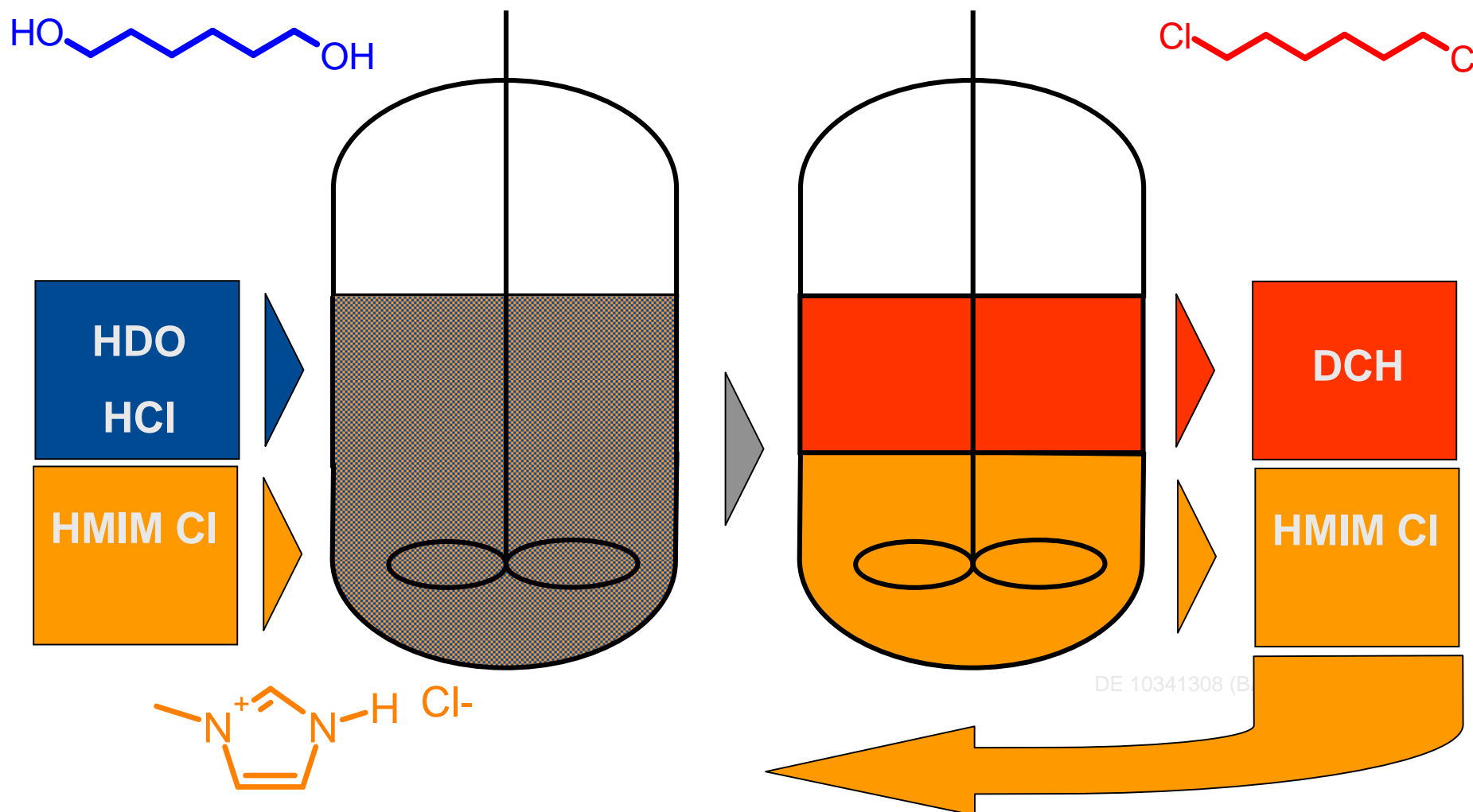
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## An alternative tool for organic chemists

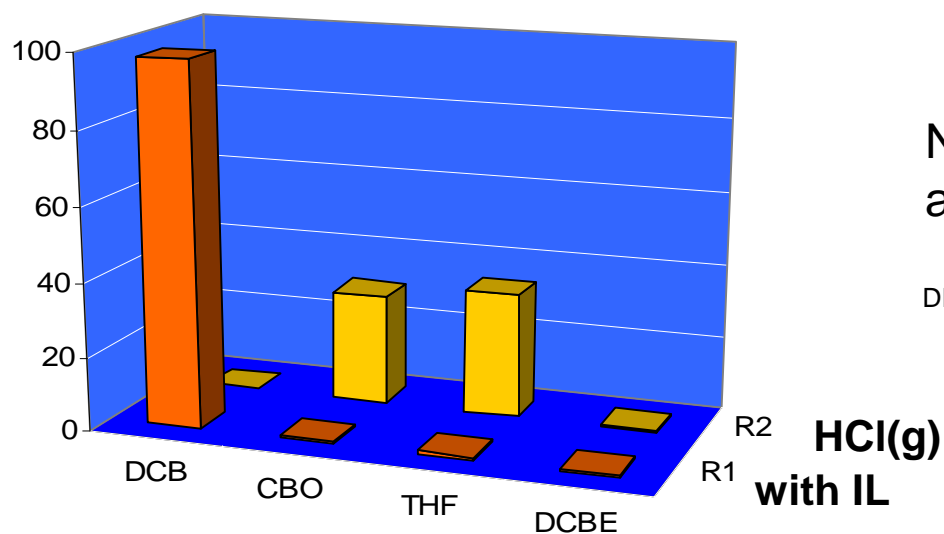
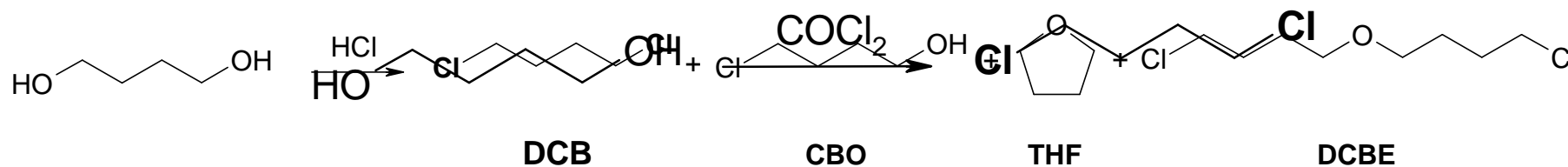


## Nucleophilic HCl: Dichloroalkanes



DE 10341308 (B)

## Nucleophilic HCl: Dichloroalkanes



Nucleophilic HCl as  
alternative to phosgene

DE 10341308 (BASF)

Ionic Liquids at BASF SE

## Nucleophilic HCl: Dichloroalkanes

 **BASF**  
The Chemical Company



**Neat Product**

**Product isolation  
by phase separation**

**Ionic Liquid**



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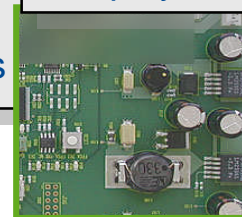
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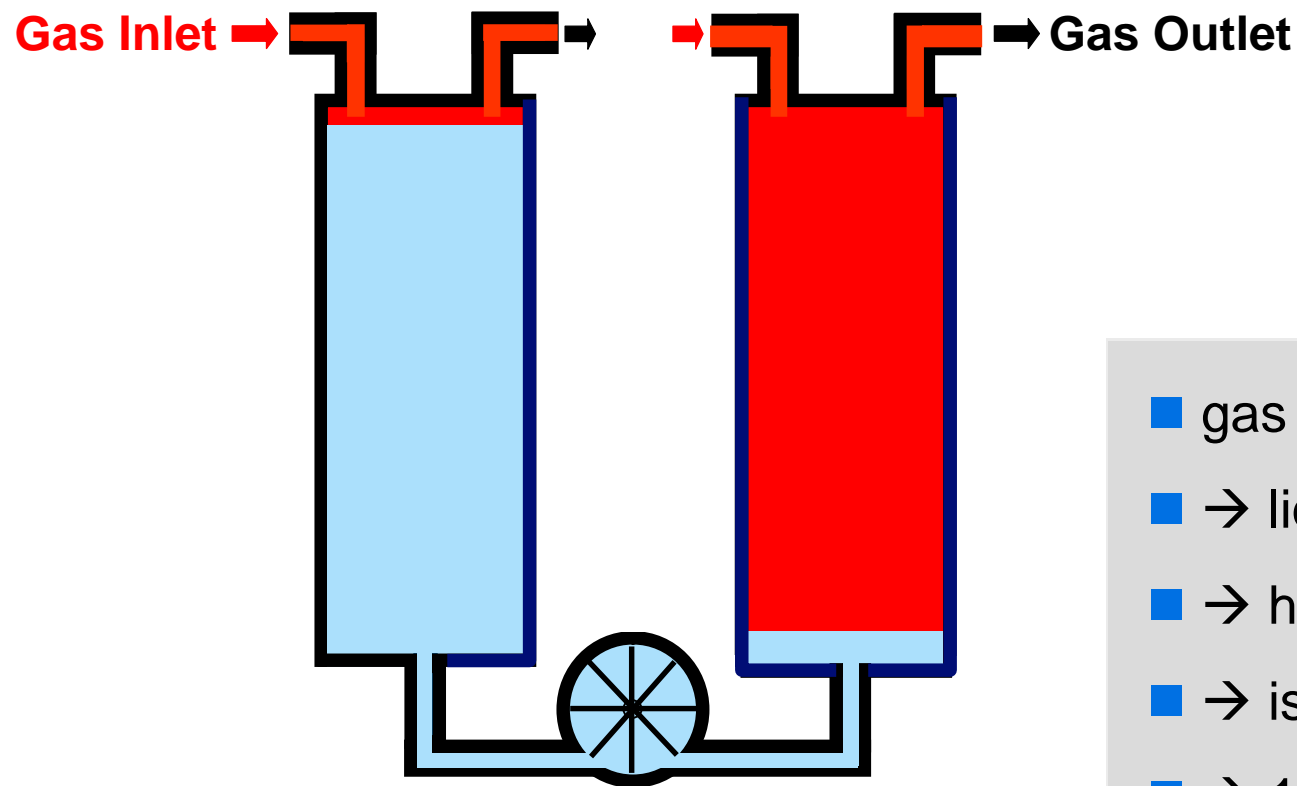


### Polymer Processing

- e.g.
- regenerated cellulose
  - cellulose derivatives
  - polymer blends



## Ionic Compressor for Gases ( $H_2$ , $CH_4$ )



- gas insolubility in IL's
- → liquid piston
- → heat removal
- → isothermal compression
- → 1 to 1.000 bars in 1 step

## Broad Range of Application Segments



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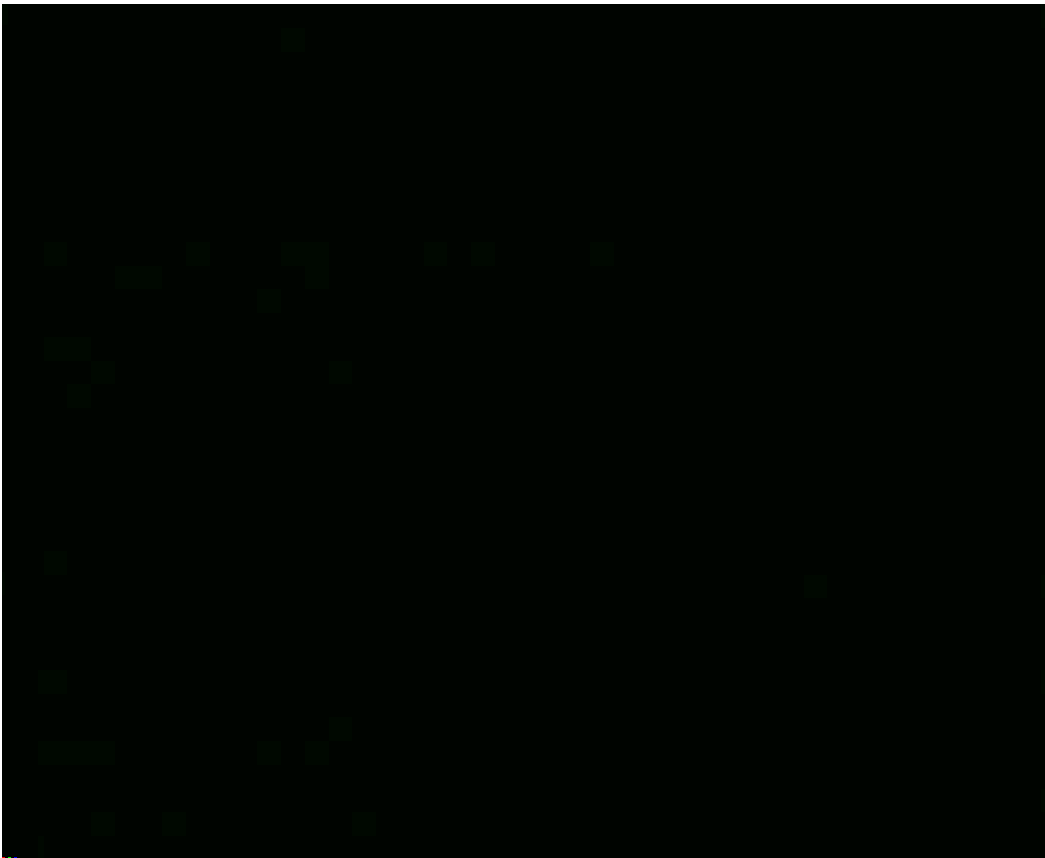


### Polymer Processing

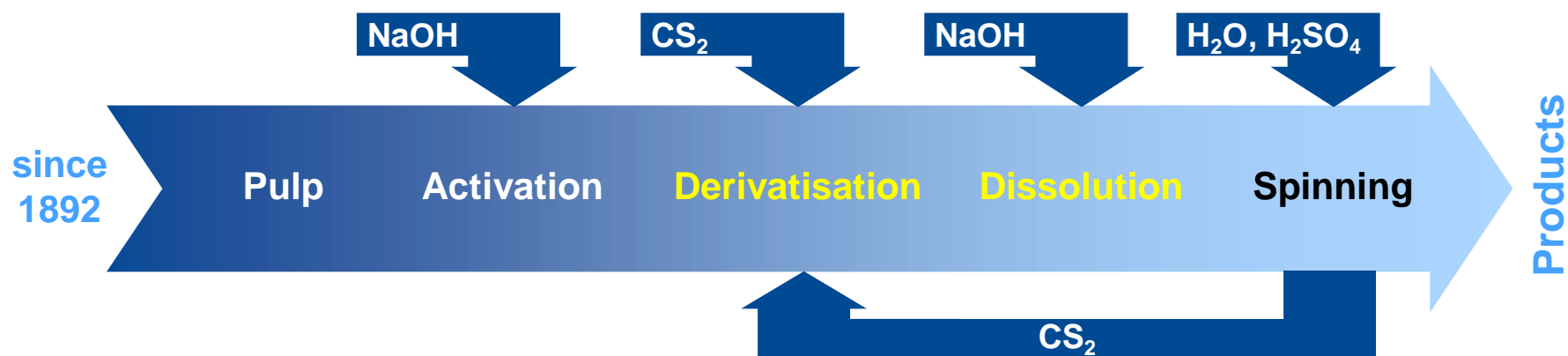
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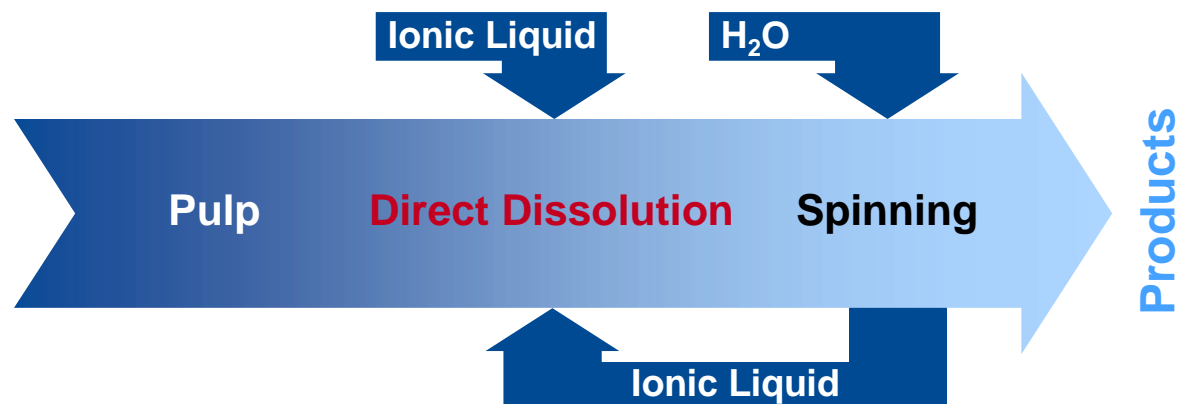
WO 2003/029.329 (03.10.2001) (Robin Rogers et.al., UoA → BASF)

- 
- 5-20% cellulose in IL's
  - specific IL's needed (anion!)
  - short dissolution time
  - DP's up to 2000
  - easy to degas
  - stable solution
  - no degradation / no ripening
  - re-precipitation with water

## Viscose Process



## Ionic Liquid Process



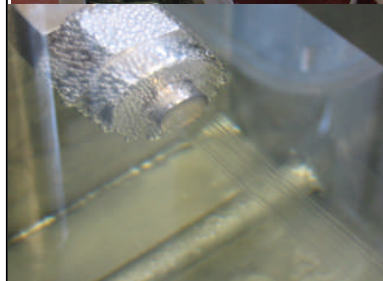
## Cellulose Reshaping: Trials @ ITCF Denkendorf



**EMIM Acetate**



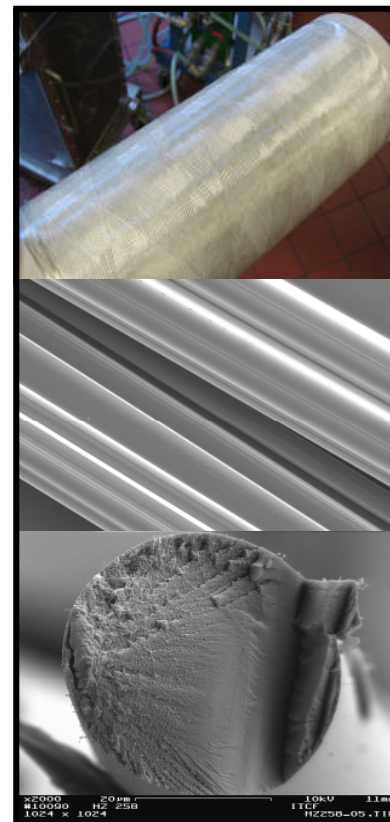
cellulose  
dissolved in IL



pilot plant  
wet spinning

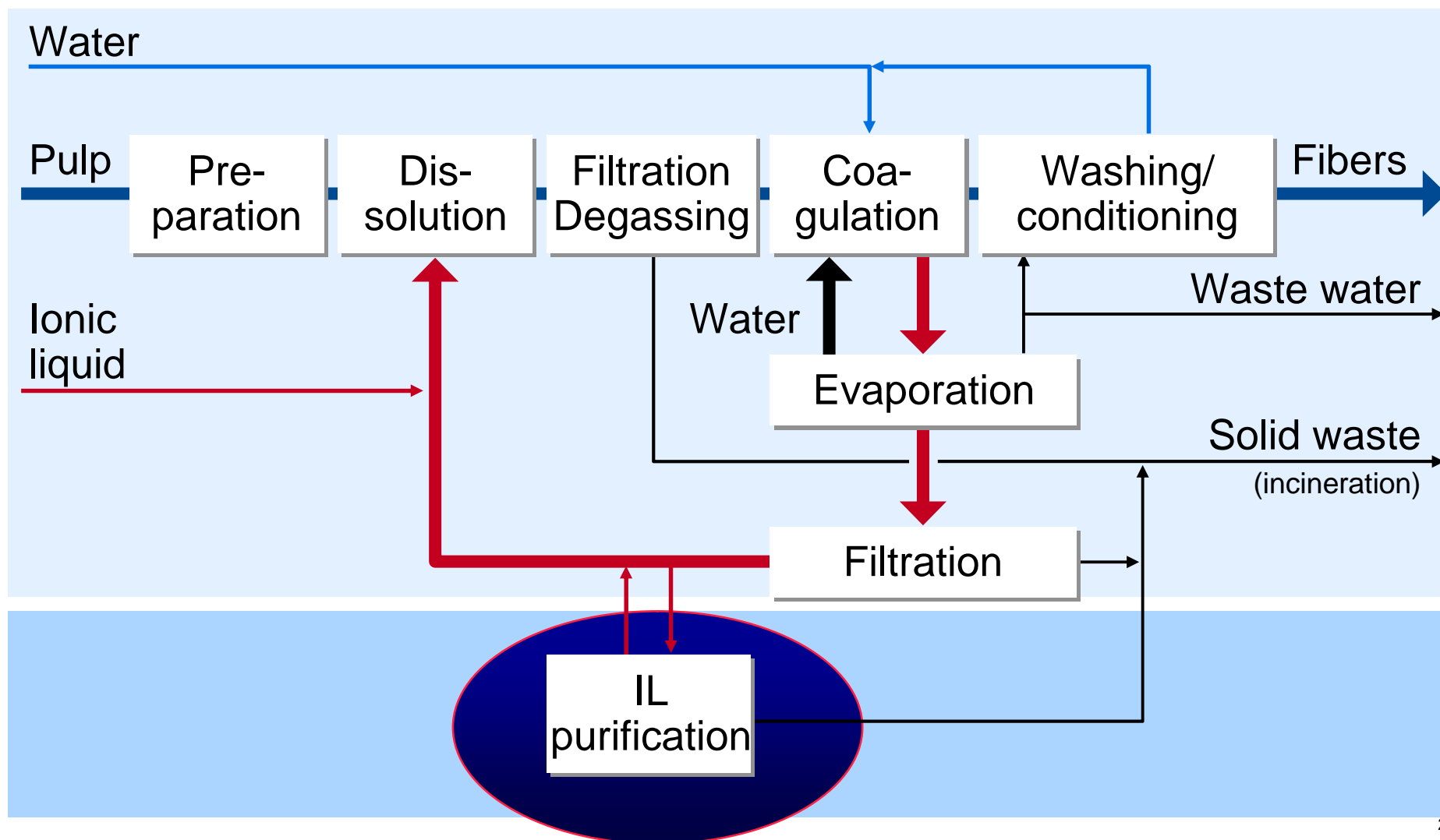


regenerated  
cellulose fibre

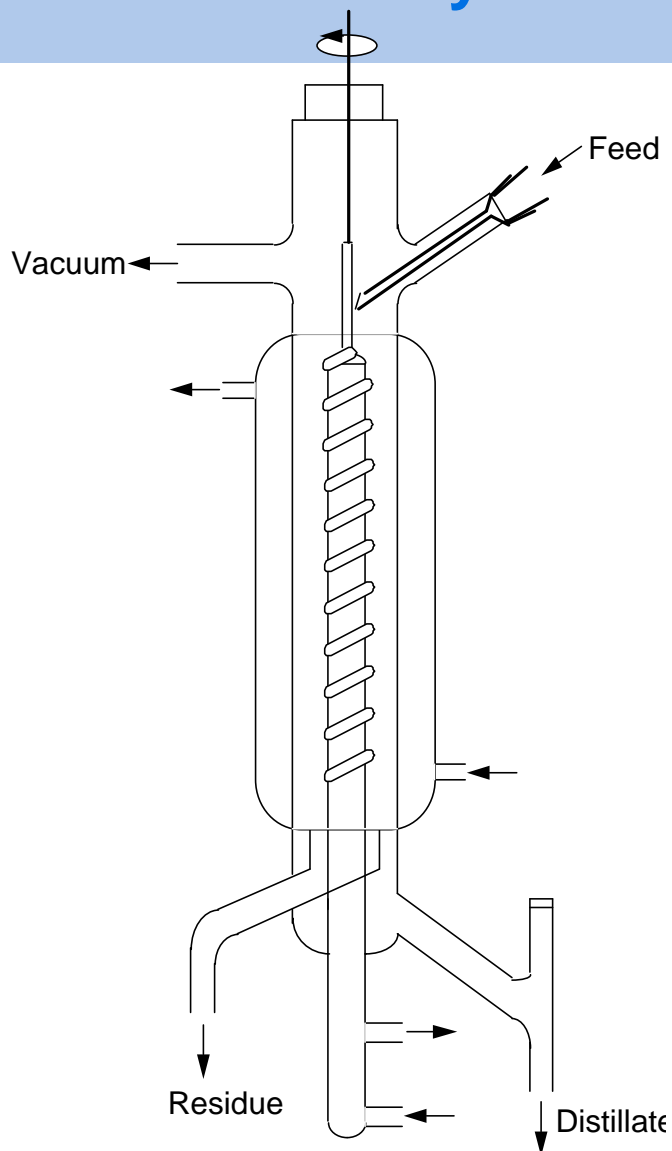




## Cellulose Reshaping



## IL Purification by short path distillation\*



IL	Structure	T <sub>dist.</sub> / °C	Yield / %
BMIMOAc	<chem>CCCC[N+]1=CNC=C1C(=O)OCC</chem>	170	> 90
BMIMOProp	<chem>CCCC[N+]1=CNC=C1C(=O)OCC</chem>	170	> 90
EMIMDEP	<chem>CC[N+]1=CNC=C1COP(=O)(OCC)OCC</chem>	250	54
EMIMN(CN) <sub>2</sub>	<chem>CC[N+]1=CNC=C1C#N[N-]#N</chem>	250	4



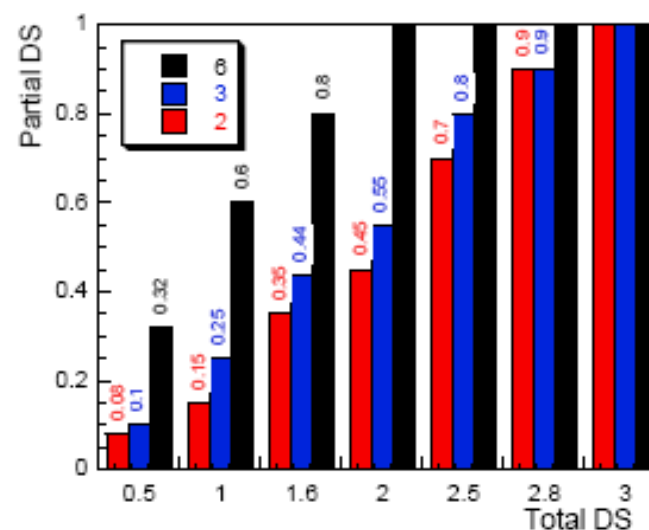
•WO 2009027250A2; Prof.Dr. W. Mormann, Siegen;  
BASF SE

## Cellulose Derivatives

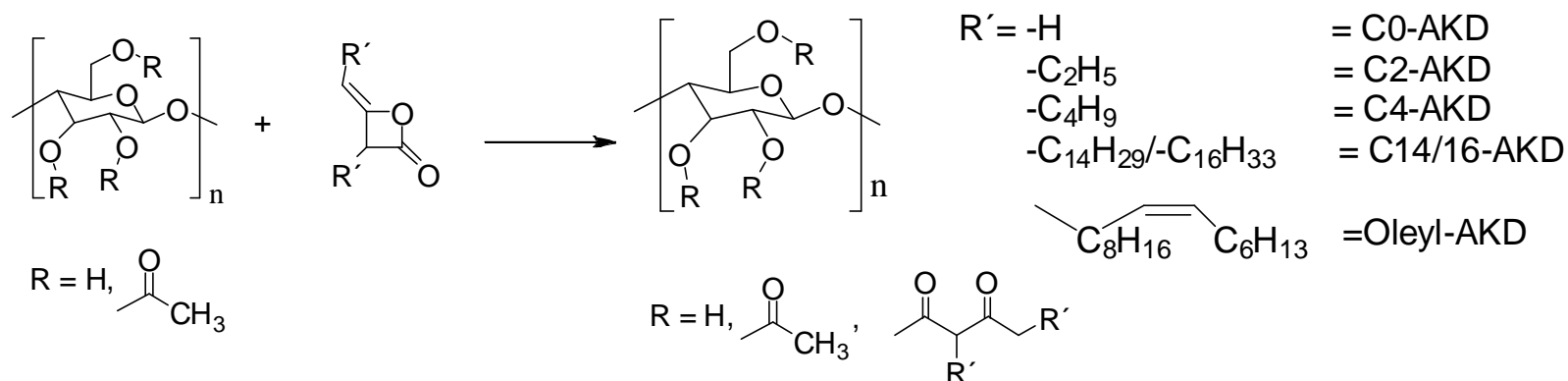


Cellulose: Avicel PH101, 10 wt-%  
Cellulose and cellulose acetates are soluble in BMIMCl

$n_{\text{AGU}}/n_{\text{Ac}_2\text{O}}$	Yield / %	$\text{DS}_{\text{NMR}}$	$\text{DS}_{\text{EA}}$
1/0,70	66	0,5	0,4
1/1,61	95	1,0	0,9
1/1,99	64	1,5	1,5
1/2,18	63	1,6	1,7
1/2,44	65	2,1	2,0
1/2,94	63	2,6	2,3
1/3,26	83	2,8	2,6
1/3,52	88	3,0	2,8



\* Cooperation with Prof. Mormann, Siegen



AKD (Löslichkeit in IL)	$n_{\text{AGU}} / n_{\text{AKD}}$	Reakt.-zeit / Std. (T / °C)	Ausb. / [%]	AcAc	
				DS <sub>NMR</sub>	DS <sub>EA</sub>
C0-AKD (Mischbar)	1/4.4	1 (100)	90	1,4	1,5
	<b>1/3.9</b>	<b>16 (100)</b>	<b>79</b>	<b>2,5</b>	<b>2,6</b>
C2-AKD (10 Mol%)	1/4.9	3 (100)	84	1,1	1,0
	<b>1/3.7</b>	<b>16 (100)</b>	<b>84</b>	<b>2,4</b>	<b>2,6</b>
C4-AKD (4 Mol%)	1/3.8	1 (100)	84	0,2	0,1
	<b>1/3.4</b>	<b>16 (100)</b>	<b>88</b>	<b>2,2</b>	<b>2,0</b>

\* Cooperation with Prof. Mormann, Siegen, WO 2008000666 A1, BASF SE

## Broad Range of Application Segments



### Chemical Processing

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- e.g.
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### Separation Processes

- e.g.
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- e.g.
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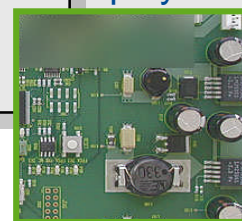
### Electronic Devices

- e.g.
- Lithium Ion Batterie
  - Super Capacitors
  - **Dye Sensitized Cells**

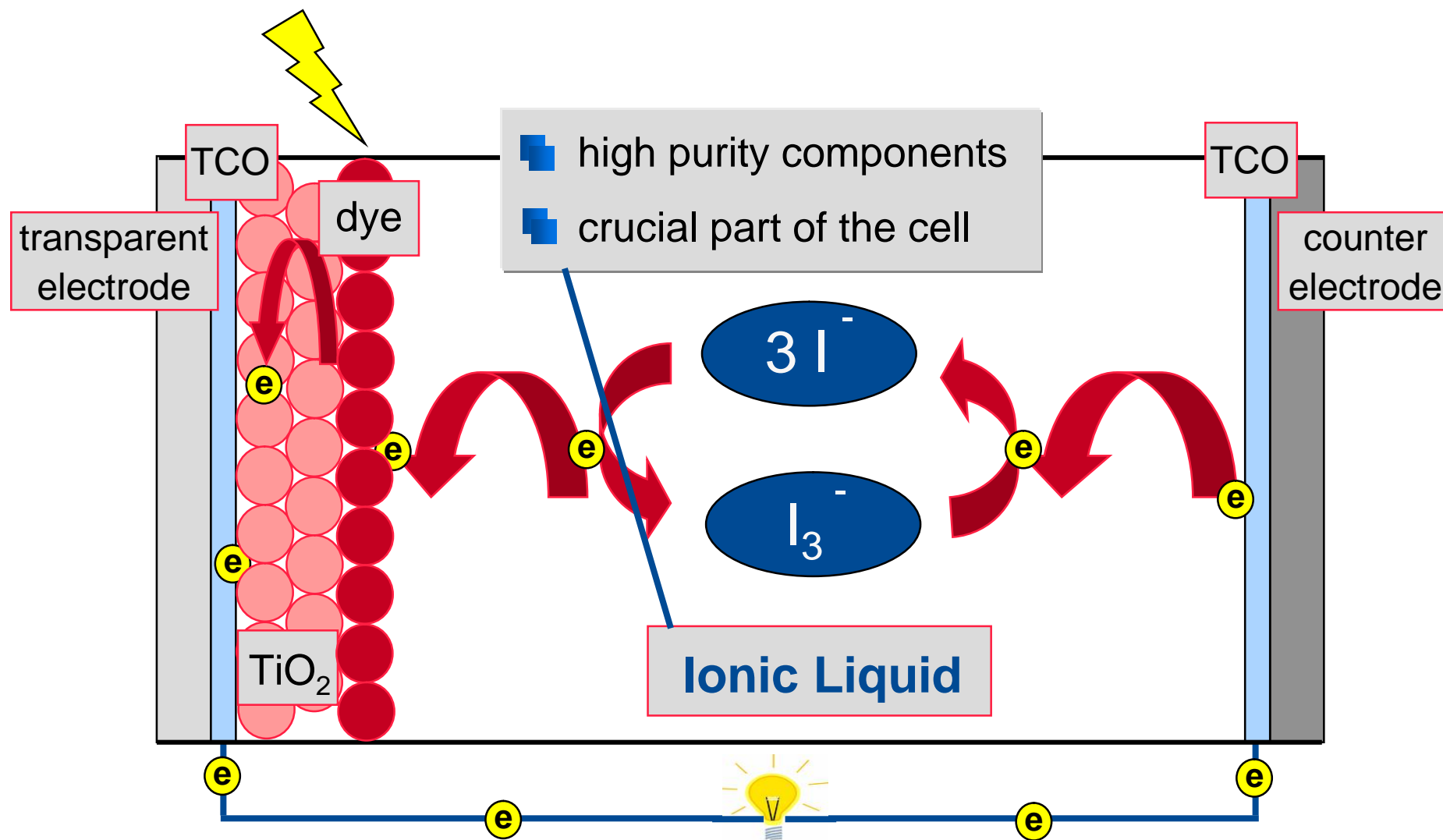


### Polymer Processing

- e.g.
- regenerated cellulose
  - cellulose derivatives
  - polymer blends



## Dye Sensitized Solar Cell (DSSC)





Ionic Liquids at BASF SE

## Dye Sensitized Solar Cell (DSSC)



G24i site in Cardiff, UK



[www.g24i.com](http://www.g24i.com)

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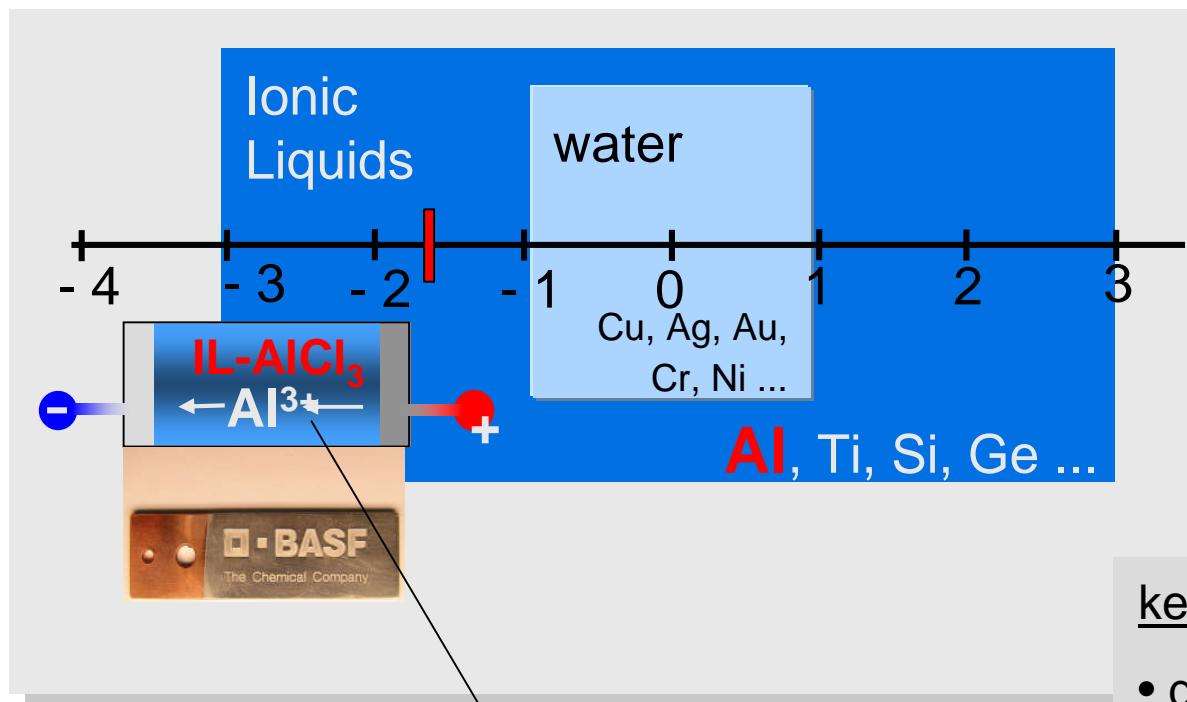


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## Elektrodeposition of Aluminum



in order to achieve a deposition with high densities, additives have to be used together with the EMIM AlCl<sub>4</sub> electrolyte

### key properties IL:

- dissolution of Aluminium species preferred for electrodeposition
- electrochemical stability  
(→ no need for other auxiliaries)
- electric conductivity

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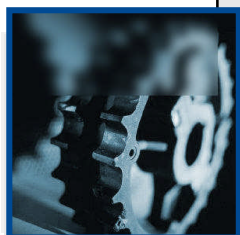
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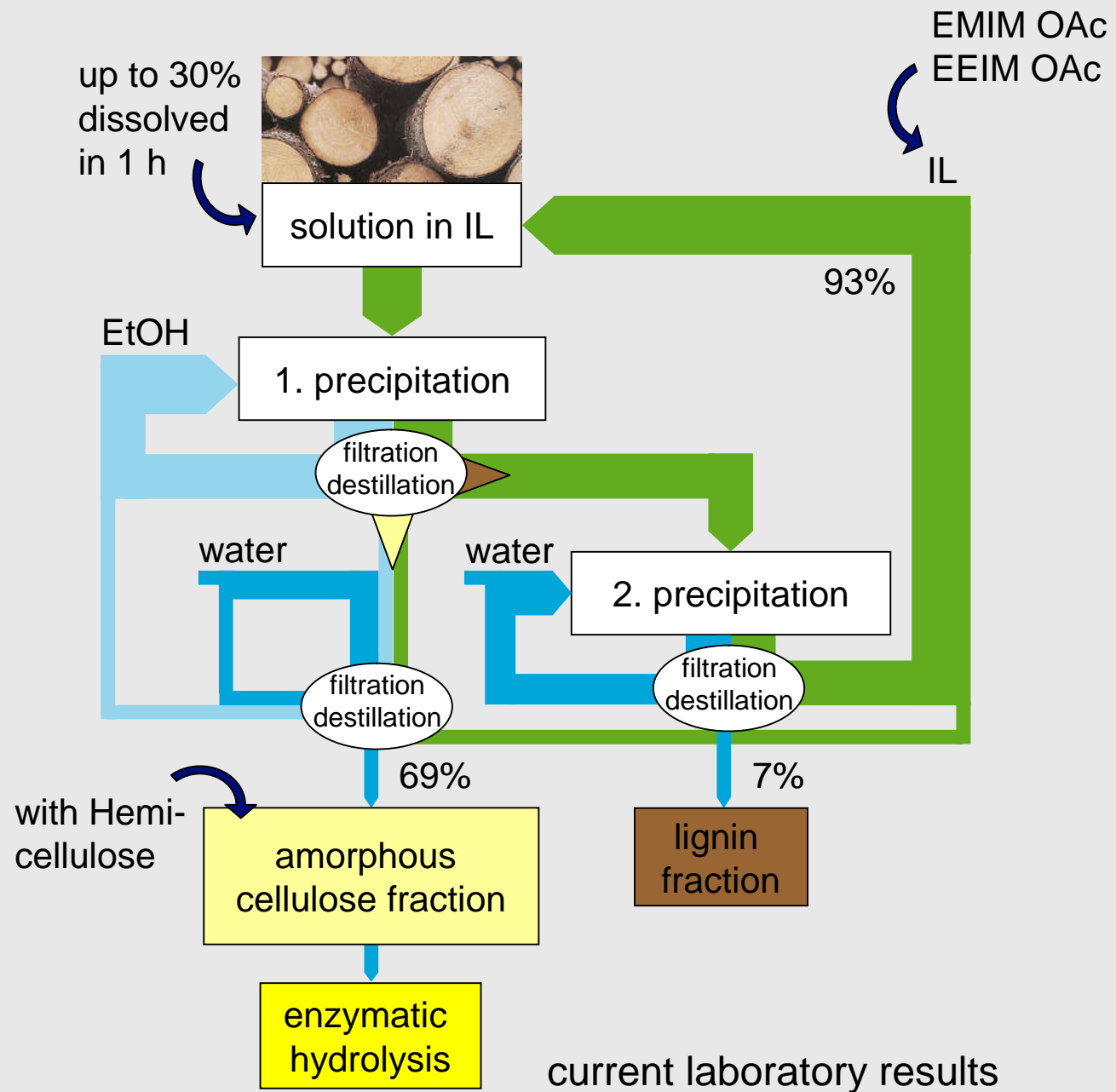
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# Biorefinery & IL

## Proof of Concept





## Broad Range of Application Segments



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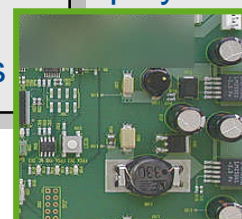
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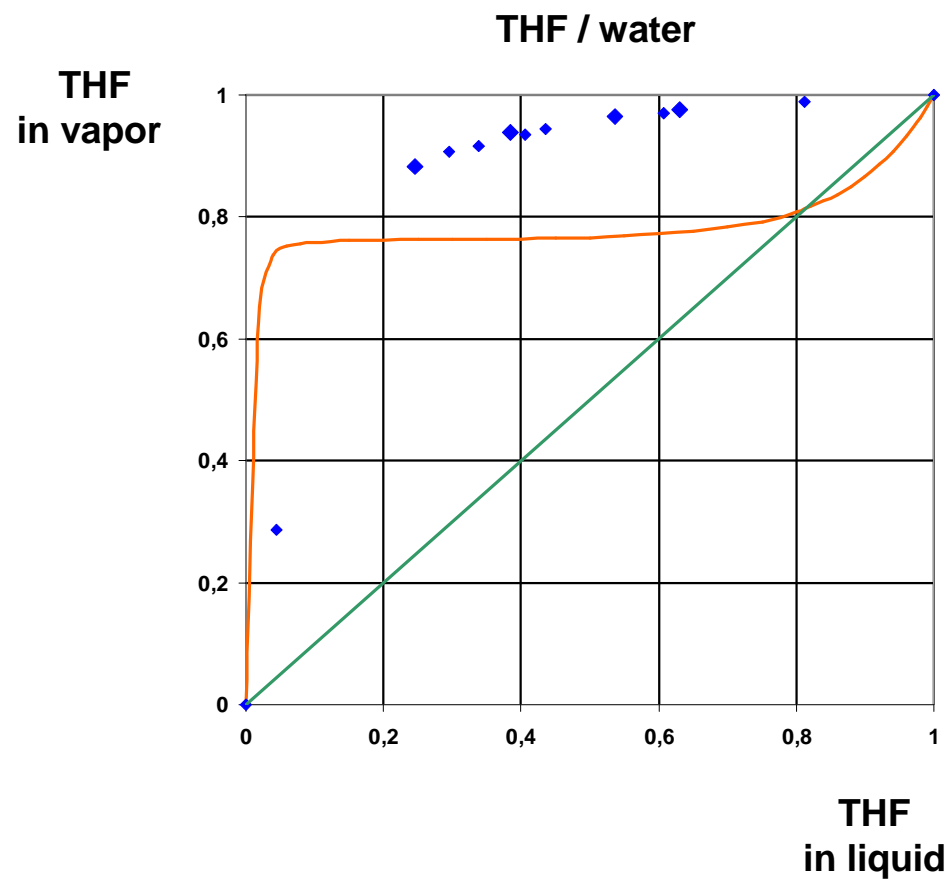
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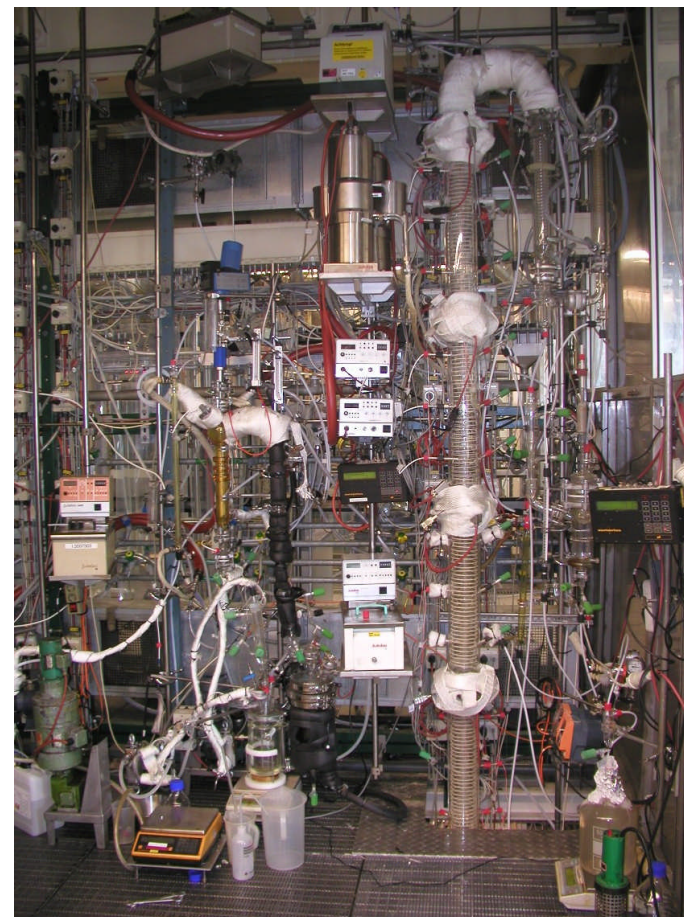
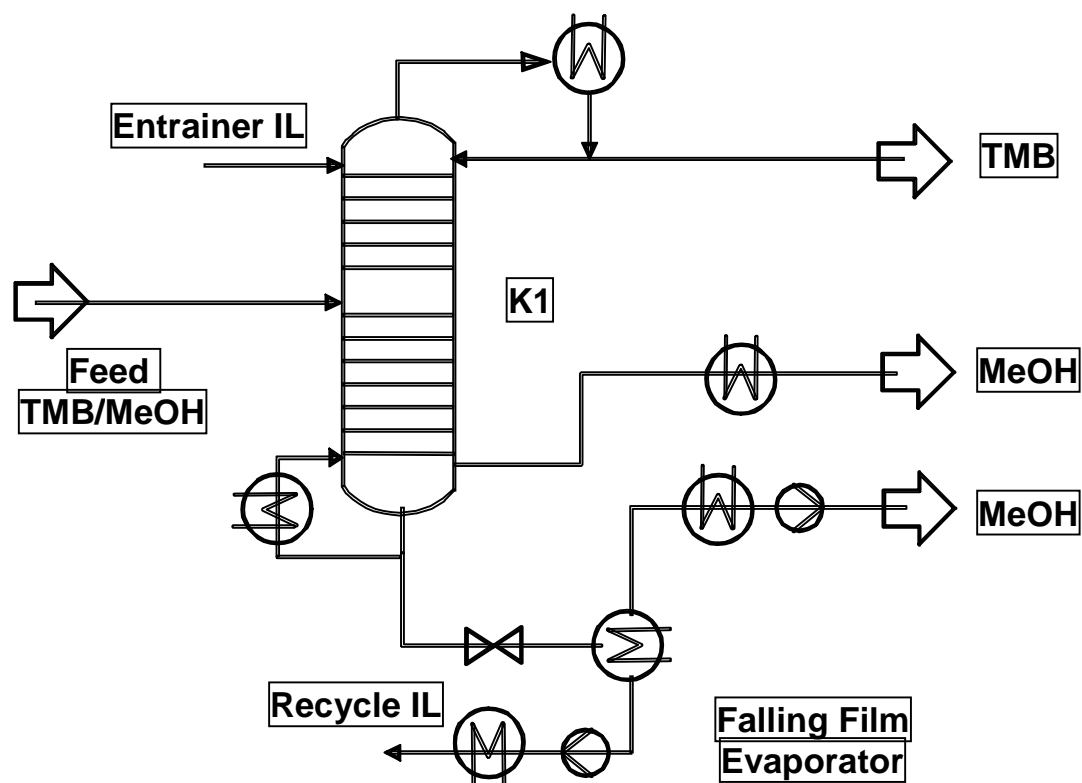




## Breaking of Azeotropes



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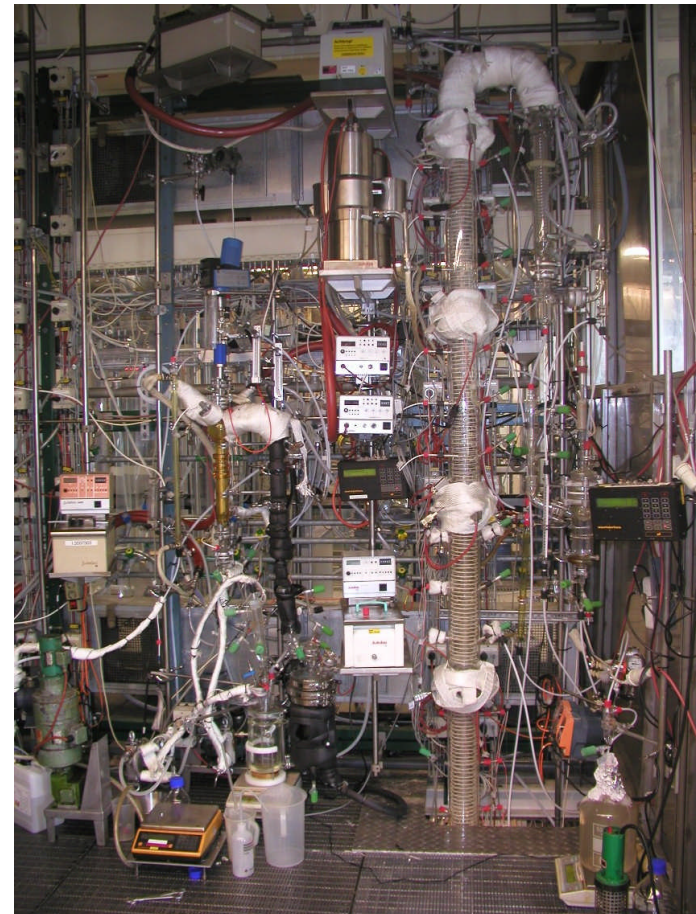


## Ionic Liquids at BASF SE

# Breaking of Azeotropes



- 3 months continuously operated
- constant performance
- no IL purge



### Comparison of Manufacturing Costs\*

Entrainer	DMF	Ionic Liquid
Purification of entrainer	Distillation	Evaporator, condensator, refrigerator
Educt losses	0%	0%
Energy	100%	63%
Environment	0%	0%
<b>Sum variable cost</b>	<b>100%</b>	<b>63%</b>
Depreciation from investment costs	100%	78%
<b>Sum total costs</b>	<b>100%</b>	<b>74%</b>

=> Use of IL leads to clear savings in invest and energy costs

=> 3 month miniplant without IL-purge

\* Assumptions: capacity 10 000 t/a



these products are regularly produced @ BASF  
in high quality and 100 kg's to tons quantities

EMIM Chloride

versatile precursor for IL synthesis

BMIM Chloride

versatile precursor for IL synthesis

EMIM Ethylsulfate

low melting point, low viscosity, high thermal stability

EMIM Methanesulfonate

low viscosity, high thermal & chemical stability

EMIM Acetate

very low melting point, low viscosity

EMIM Methylcarbonate

versatile precursor for IL synthesis

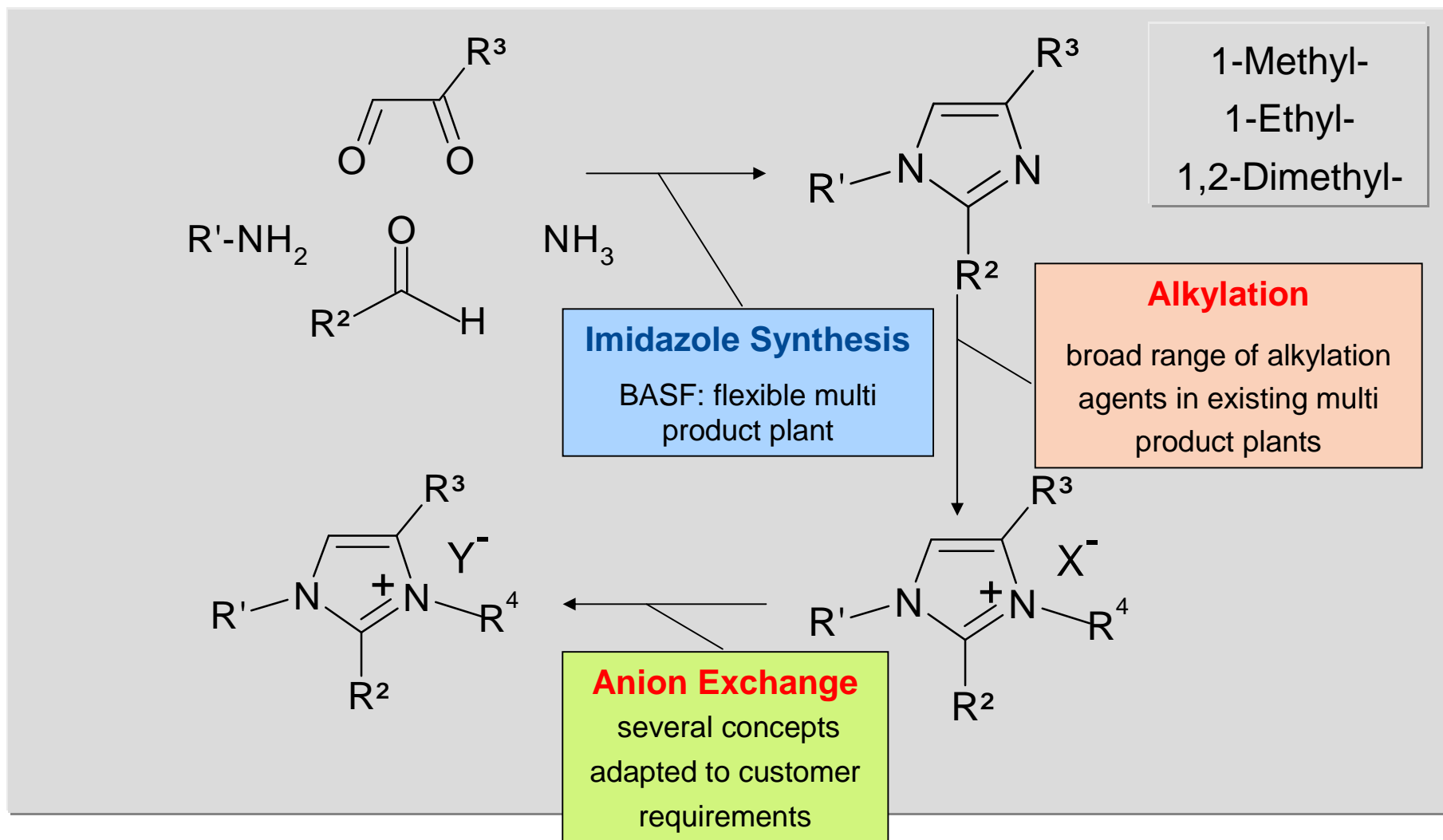
EMIM TFSI \*)

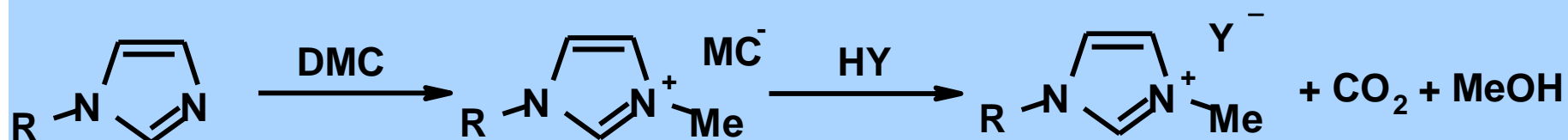
low viscosity, high electrochemical stability, hydrophobic

*TFSI = bis(trifluoromethanesulfonyl)imide*

*\*) not available in the US*







WO (proionic / BASF) 2005 / 021.484

**pro ionic**

→ industrial scale synthesis developed together with pro ionic

advantages:

easy access to a broad range of IL's with different anions

very broad flexibility by utilizing:

HY = Brønsted-Acids or Ammonium Salts

purity profile:

in principle halide free synthesis route (corrosion !)

resulting in high purity IL's





experience: no single IL meets all criteria  
requested for Engineering Fluids

→ range of products specifically adopted to  
customer needs

- optimization of performance properties  
(esp. viscosity / viscosity index, lubrication properties)
- material compatibility (e.g. corrosion behaviour)
- environmental aspects (e.g. toxicity, biodegradability)

### First toxicological assessments

**cation:** toxicity & ecotoxicity increases with the length of the alkyl chains  
this is more or less independent from the cation chemistry  
→ preferred: Ethyl Methyl Imidazolium (EMIM) cation

**anion:** first indication can be taken from toxicity of e.g. alkali metal salts  
e.g. chloride, methylsulfate, acetate → non toxic  
fluorinated anions e.g. bis(trifluoromethanesulfonyl)imide → toxic

- dermal toxicity of all IL's tested so far is considerably low
- so far no effects on mutagenicity observed
- most IL's are not readily biodegradable;  
unless they contain functional groups (e.g. cholinium)

## BASF's Offers

**Supply**  
BASIONICS™

supply of standard or customized  
Ionic Liquids

**Supply  
Contract**

**License** on BASF's  
IL know how

access to BASF's IP and know how  
on Ionic Liquids  
(incl. BASIL™ processes)

**License  
Agreement**

**Joint  
Development**

jointly develop new products or  
processes by utilizing IL's

**Joint  
Development  
Agreement**