

GEFÖRDERT VOM



Bundesministerium
für Bildung
und Forschung



First results of a collaboration between CNRS Strasbourg and Forschungszentrum Jülich

Andreas Wilden

German-French research for nuclear safety: Chemistry of
the f-elements

IPHC, Strasbourg, 23rd February 2012

Ionic liquids – definition and properties

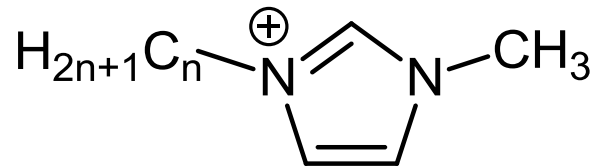
- Salt with a melting point below 100°C
- Combination of (org.) cation and anion

- + Non flammable
- + Non volatile
- + Resistant against radiolysis
- Often highly viscous
- expensive

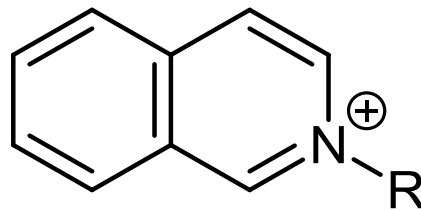
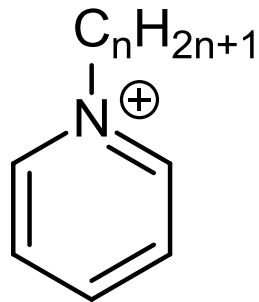
- Nearly infinite number of combinations
- Synthesis of tailored “Task-specific” ionic liquids is possible

Classical ionic liquids

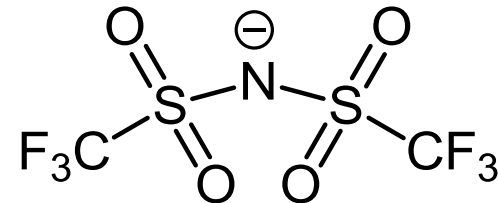
Cations



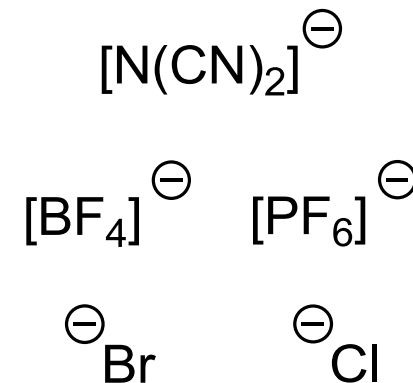
e.g. [bumim]⁺
(butyl-methyl-imidazolium)



Anions



[Tf₂N]⁻
(bis-trifluoromethyl-sulfonyl
amide)

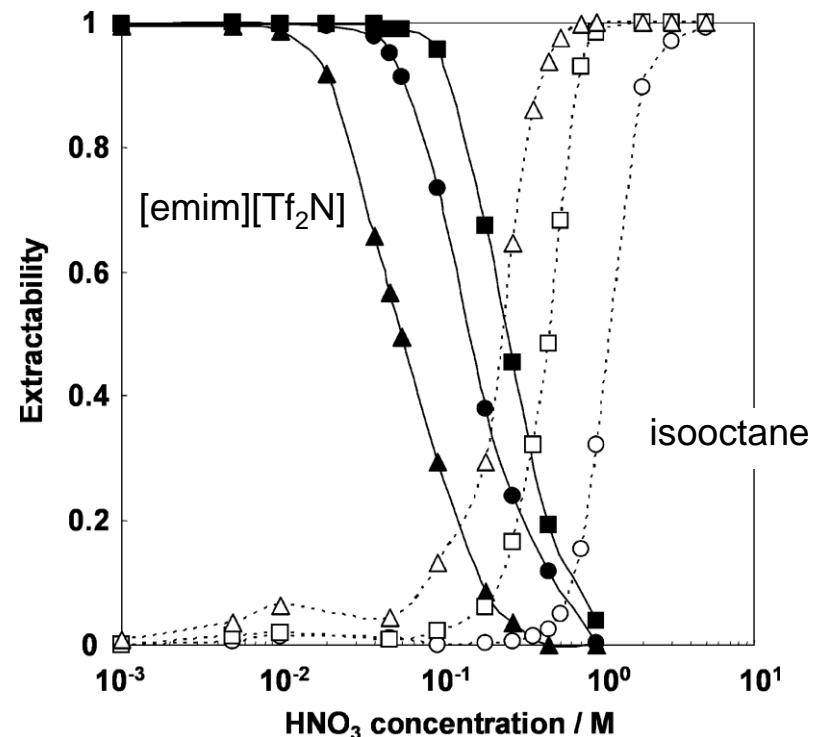


Surprising extraction in ionic liquids

Extraction of lanthanides using TODGA

in [C2mim][Tf₂N] (closed symbols and solid line) or in isoctane (open symbols and broken line)^[1]

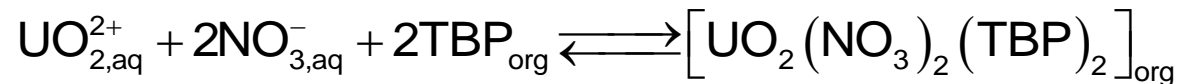
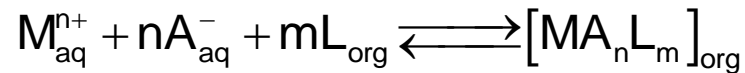
- Inverse HNO₃ dependency!
- Different selectivity
- Lu > La > Eu in IL
- Lu > Eu > La in isoctane



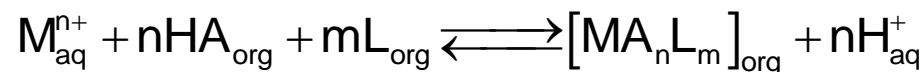
[1] Shimojo, K.; Kurahashi, K.; Naganawa, H. Dalton Trans. **2008**, (37), 5083-5088.

Typical extraction mechanism in common org. diluents

1) Solvation mechanism



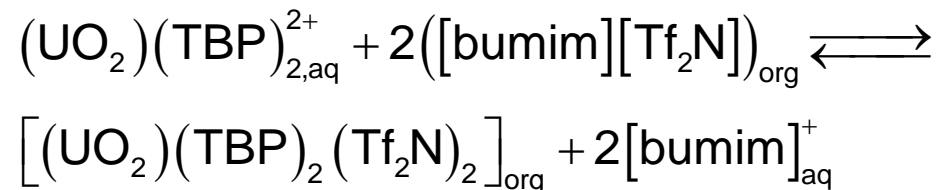
2) Ion exchange mechanism



- Neutral complexes in the org. phase!

Unconventional extraction mechanism in unconventional diluents

- In early studies on metal extraction into IL phases, also the formation of neutral complexes was assumed, following the solvation mechanism^[2]



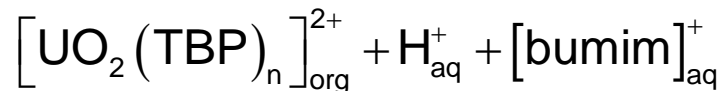
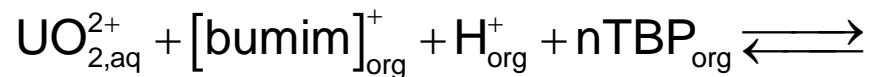
- Further studies showed that this assumption was not in line with experimental results from UV-Vis studies and $[\text{HNO}_3]$ dependency at low nitric acid concentration^[3]
- Charged complexes in the IL phase!

[2] Dietz, M. L.; Stepinski, D. C. *Talanta* **2008**, 75 (2), 598-603.

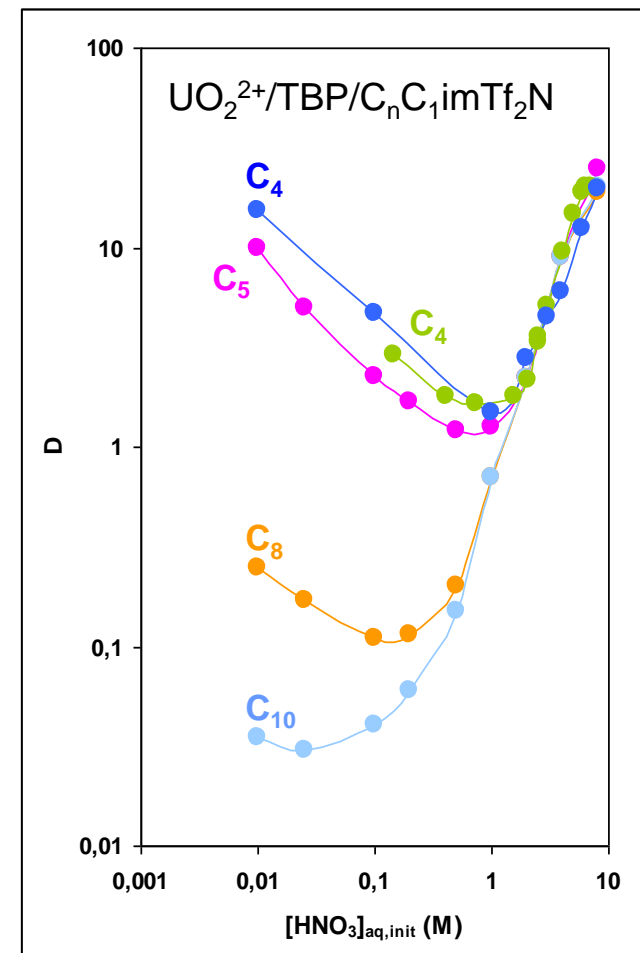
[3] Billard, I.; Ouadi, A.; Jobin, E. et al. *Solvent Extr. Ion Exch.* **2011**, 29 (4), 577-601.

Updated extraction mechanism – 2 regimes of extraction

- Low HNO_3 concentration – Regime I



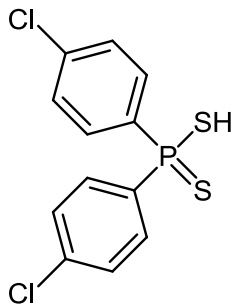
- High HNO_3 concentration – Regime II



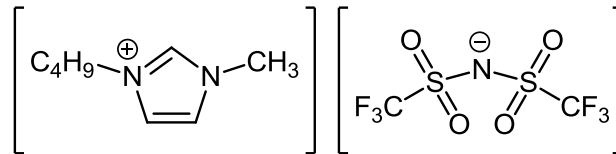
“Boomerang”-shape curve^[3] 7

My work in Strasbourg (19.10.-18.11.2011)

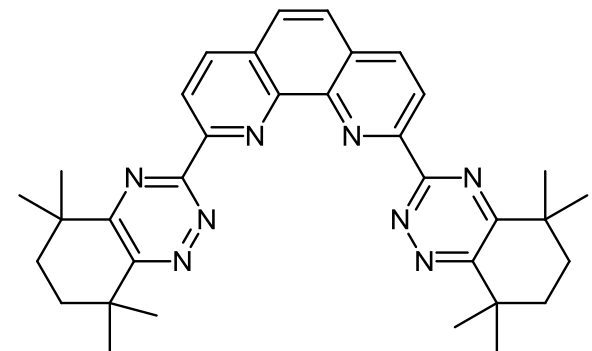
- Solubility tests of [bumim][Tf₂N] in org. diluents
- Solubility tests of extractants in [bumim][Tf₂N]
- UV-Vis studies (protonation of ligands)
- Liquid-liquid extraction using extractants dissolved in [bumim][Tf₂N]
- Modelling



BCDTP
Bis(4-chlorophenyl)-
dithiophosphinic acid

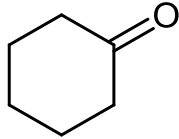
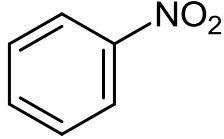


[bumim][Tf₂N]
[3-butyl-1-methyl-1*H*-imidazolium]
[bis((trifluoromethyl)sulfonyl)amide]

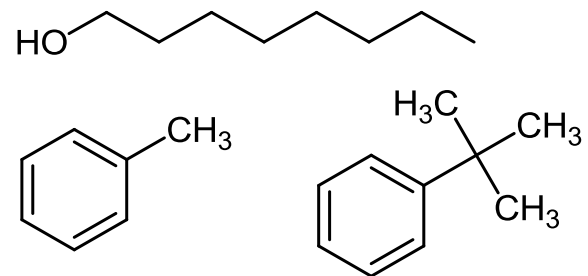


CyMe₄BTPPhen
2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-
tetrahydrobenzo[e][1,2,4]triazin-3-yl)-1,10-
phenanthroline

Solubility of [bumim][Tf₂N] in (org.) diluents

- High solubility
 - Cyclohexanone 
 - Nitrobenzene 
- Low solubility
 - TPH / Exxsol-D80 / kerosene

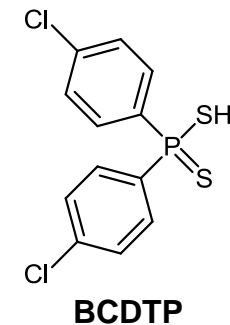
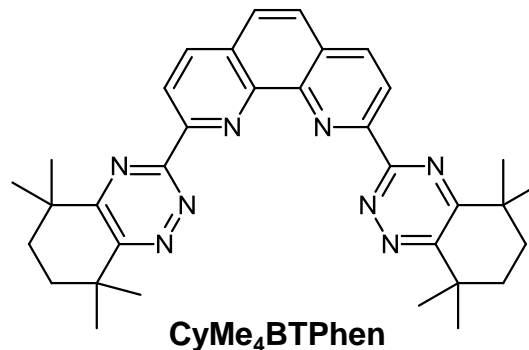
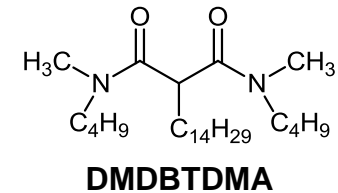
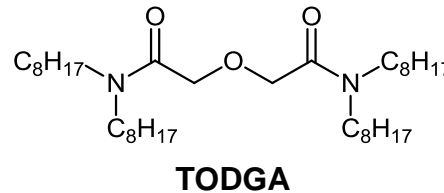
- 1-octanol
- Toluene / tert-butylbenzene
- H₂O



Solubility of extractants in [bumim][Tf₂N]

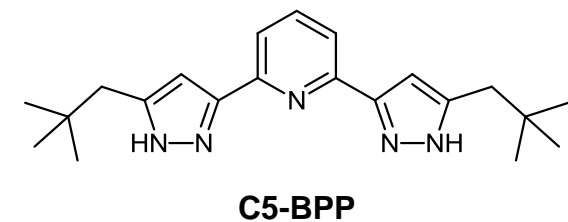
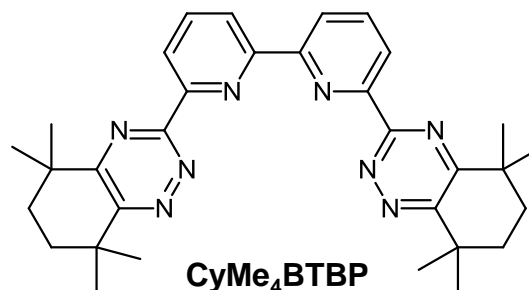
- High solubility

- TODGA
- DMDBTDMA
- BCDTP
- CyMe₄BTPPhen



- Low solubility

- CyMe₄BTBP
- C5-BPP
- aq-BTP

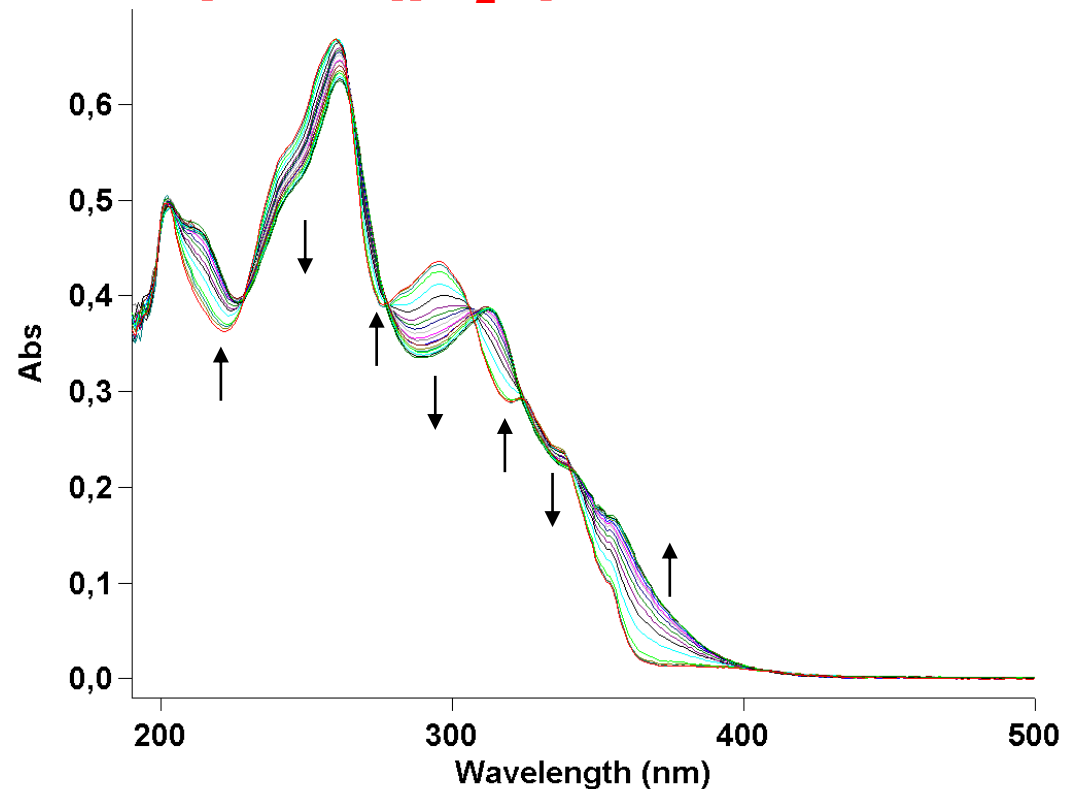
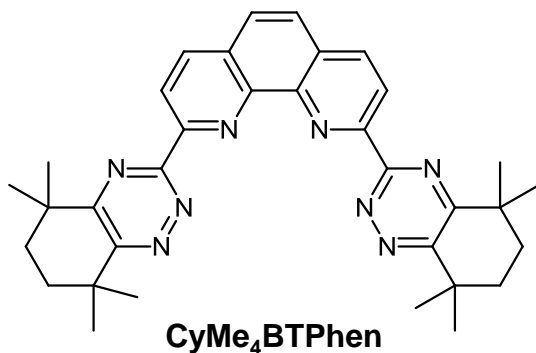


Modelling/Fitting of the extraction results I

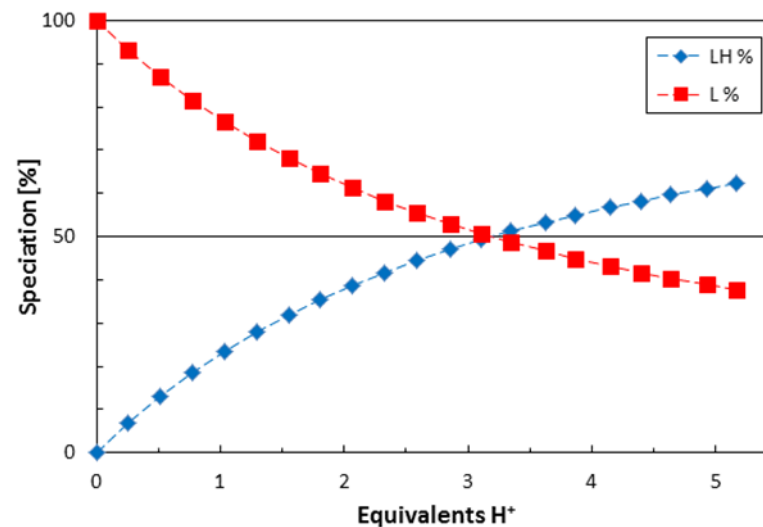
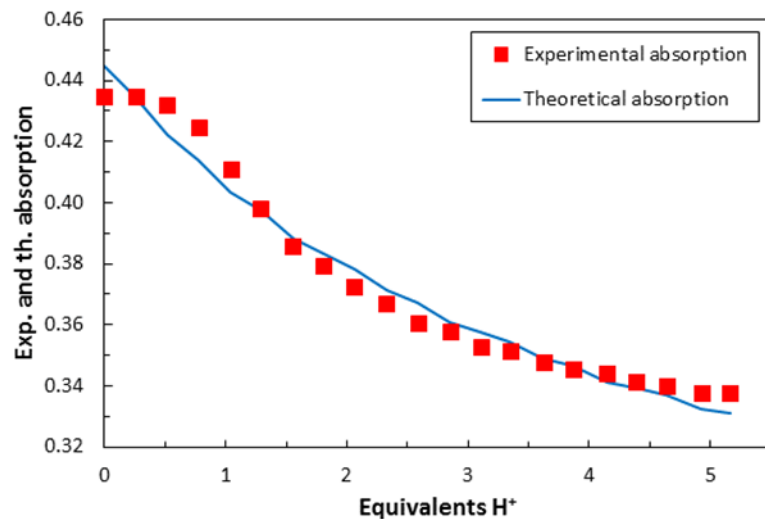
- Extraction is a function of
 - Chemical complex formation constant (mass action law)
 - $AmL_{x,org}$
 - $Am(NO_3)_{x,aq}$ → **tabulated**
 - (Free) Ligand concentration
 - Protonation of the Ligand? → **UV-Vis**
 - HNO_3 concentrations (aq+org)
 - $H^+ / NO_3^- / HNO_3$ -dissociation → **Titration / table**
 - $[bumim^+]_{aq}$ concentration → **NMR**
 - $[Tf_2N^-]_{aq}$ concentration → **NMR**
 - H_2O concentration (org) → **Karl-Fischer**

UV-Vis studies

- No observable change in the UV-Vis spectra (protonation) of BCDTP or CyMe₄BTPPhen in [bumim][Tf₂N]
- CyMe₄BTPPhen was studied in **methanol** instead



UV-Vis studies – data fitting

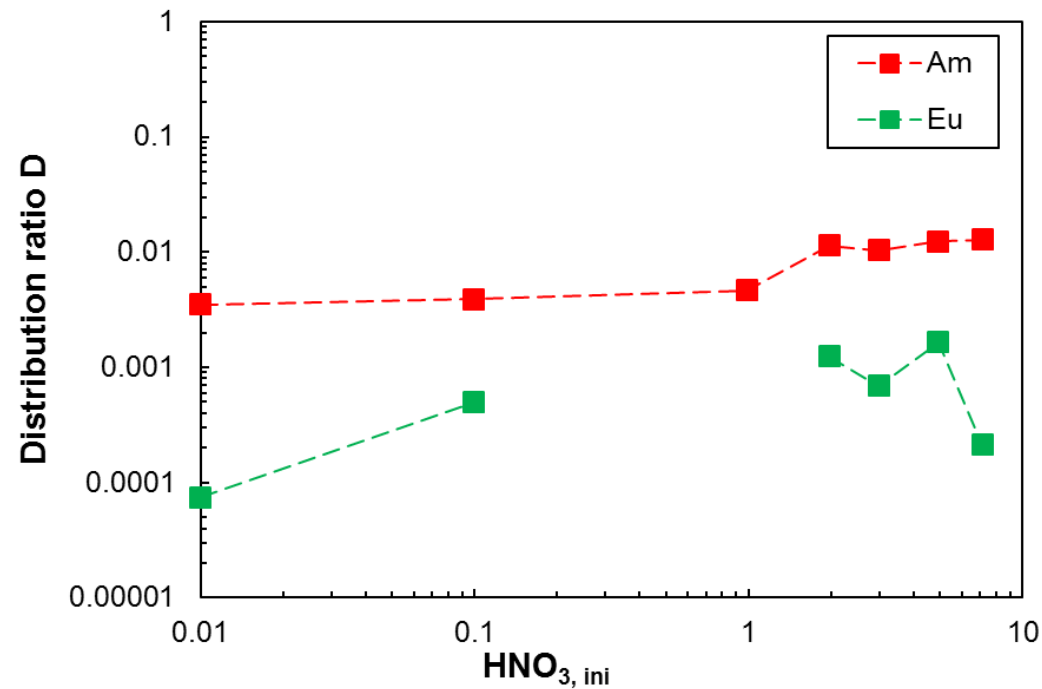
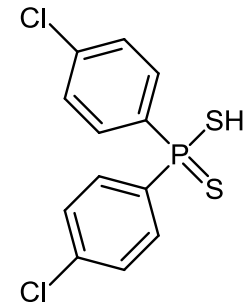


- Our $\log K_a = 4.48$
- Lit.: $\log K_a = 3.1$
(NMR in MeOD)^[4]

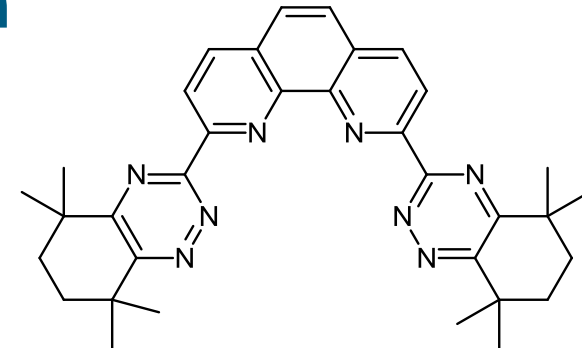
Variable	Calculated value	Experimental value
K	29987	
ϵ_{LH^+}	23023	
ϵ_L	34466	33703

Extraction results BCDTP

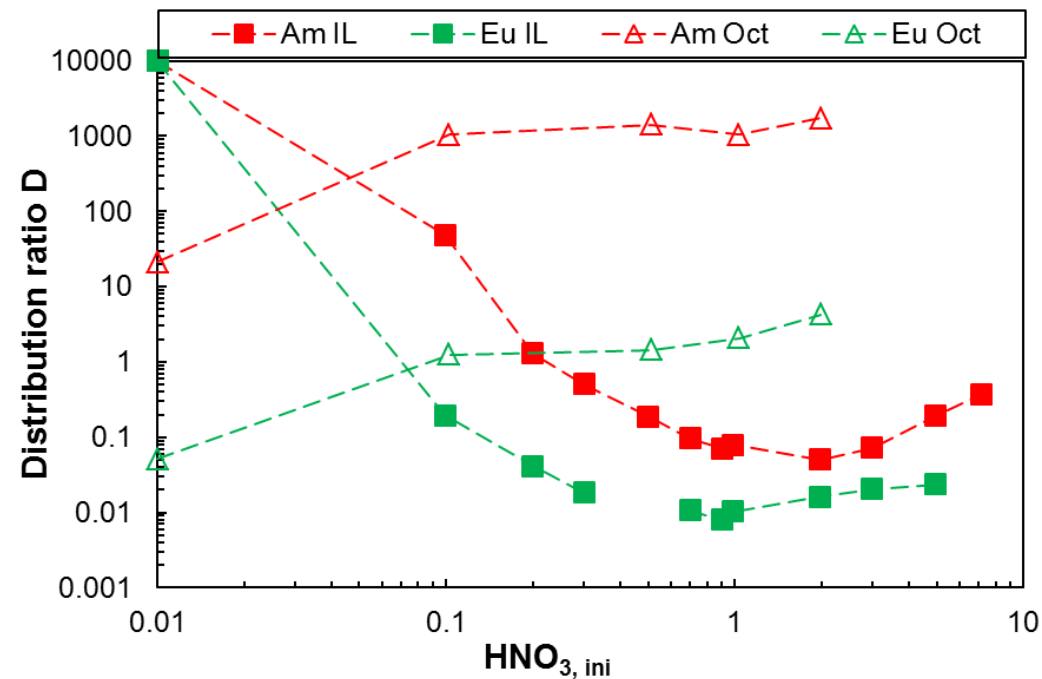
- Am/Eu tracer
 - Extraction into [bumim][Tf₂N]
 - Without synergist
 - **No extraction!**
-
- Probably a synergist is required



Extraction results CyMe₄BTPhen

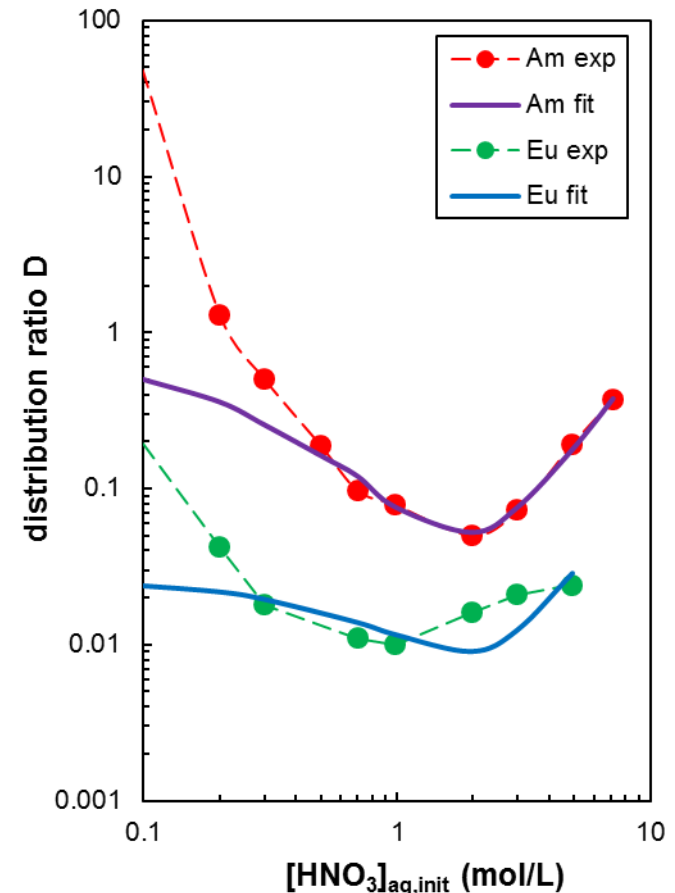


- Am/Eu tracer
- Extraction into [bumim][Tf₂N]
- **Boomerang shape curve**
- SF up to 250
- At 0.01 mol/L HNO₃ quantitative extraction
- Inverse HNO₃ dependency!



Modelling/Fitting of the extraction results II

- First rough estimation model
 - Estimated complexation constants
 - Only one mechanism tested
- Good Am fit in region II
- Not so well fit in region I
 - Activity coefficients of most species unknown
 - SIT: most species unknown
 - More exp. data is needed
- Eu fit generally not good
 - Distribution ratios quite low



Conclusions / Outlook

- Ionic liquids provide unusual properties
 - Enhanced safety
 - Surprising extraction results
 - Different mechanisms
- Interesting preliminary results were obtained
 - Extraction experiments using BCDTP and CyMe₄BTPhen
- Modelling/Fitting of experimental data
 - Further improvement of the model
 - SIT parameters
- Future cooperation
 - Further extraction experiments
 - Determination of the extraction mechanism

Acknowledgements

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