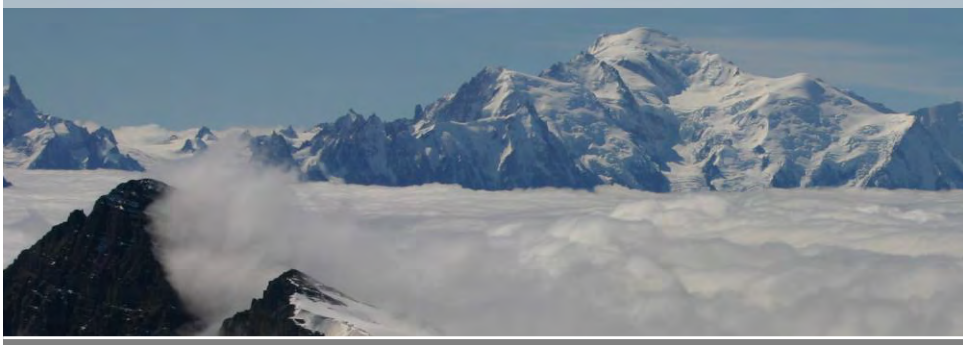
Prof. Ingo Krossing
Lehrstuhl für Molekül- und Koordinationschemie
und Freiburger Materialforschungszentrum FMF



What can we learn from Ionic Liquids with Weakly Coordinating Anions …

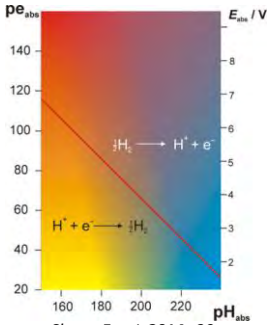
Rostock, SPP-IL-Meeting - 19.02.2015

Mont Blanc seen from Dents de Midi, CH.

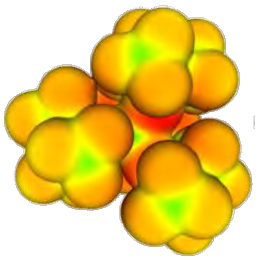
Ionic Systems:

- **Ionic Liquids** and **Electrolytes**
- **Cationic** Main Group Compounds/Clusters
- **Cationic** Transition Metal Complexes
- **Cationic** Brønsted Acids and Oxidants
- **Carbocations**

The Protoelectric Potential Map

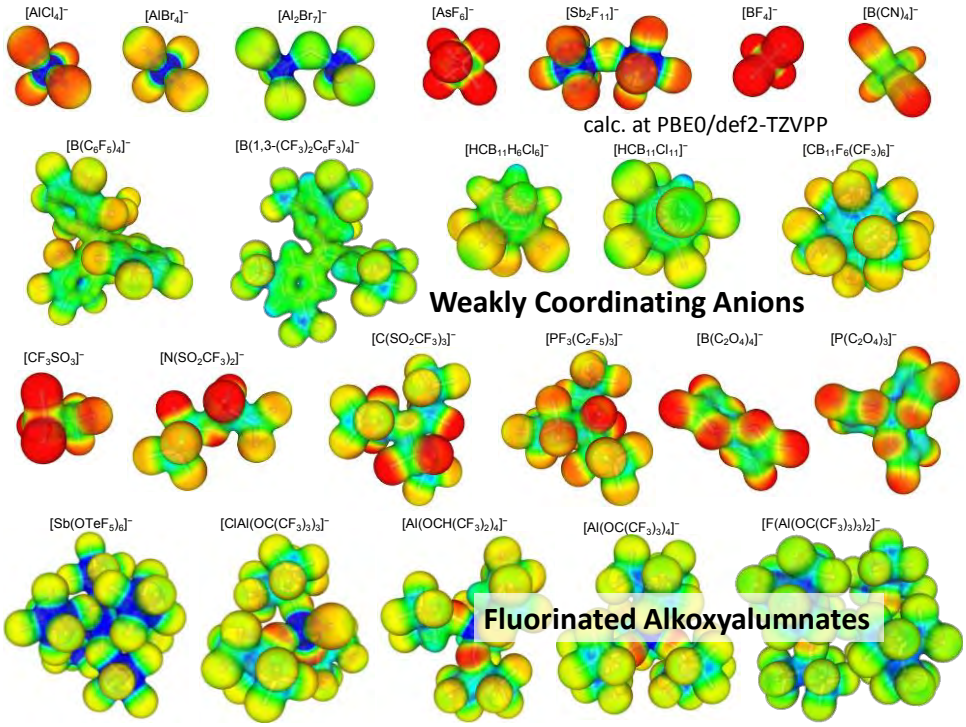


Chem. Eur. J. **2014**, *20*, 4194-4211 (**VIP-paper**).

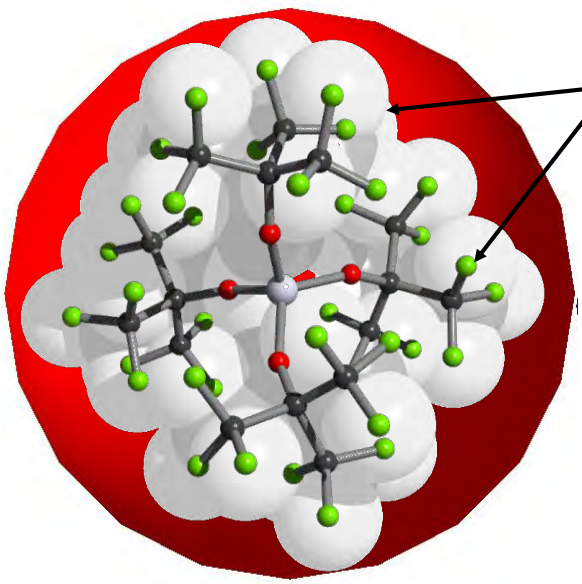


Weakly Coordinating Anions

I. Krossing, I. Raabe, *Angew. Chem.* **2004**, *116*, 2116-2142.
I. Krossing, A. Reisinger, *Coord. Chem. Rev.* **2006**, *250*, 2721.
T. Engesser, I. Krossing, *Coord. Chem. Rev.* **2013**, *257*, 946-955.
I. Krossing, *Compr. Inorg. Chem. II*, Vol. 1, Chapter 1.26, **2013**, 681-705.



[Teflon]$^-$...?



Surface C-F Bonds:

=> Teflon…!

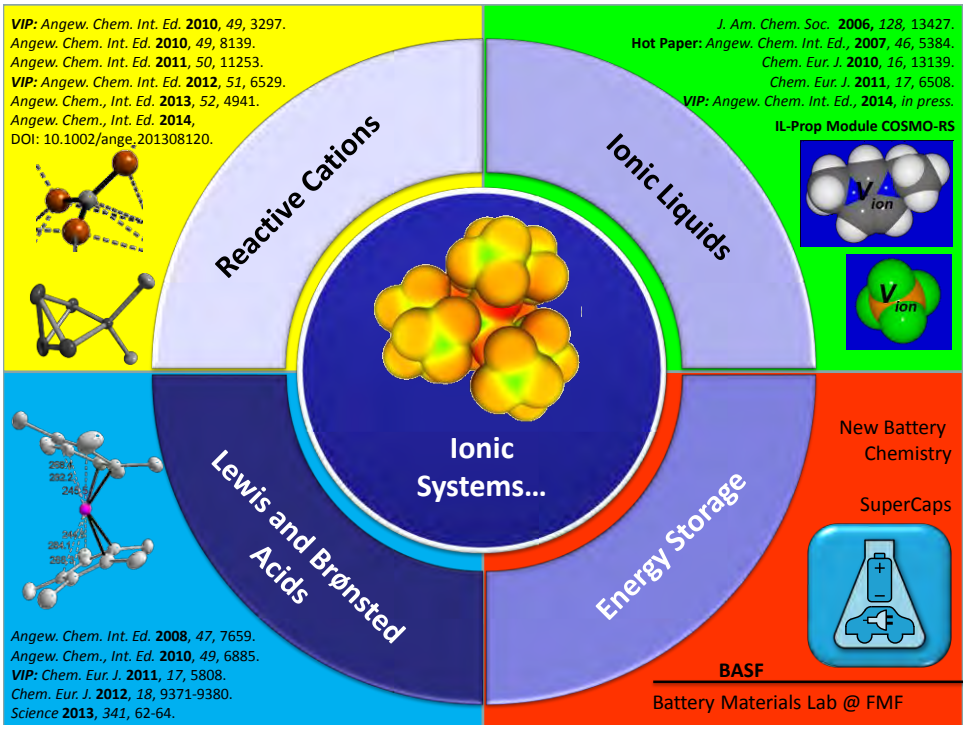
Large Volume:

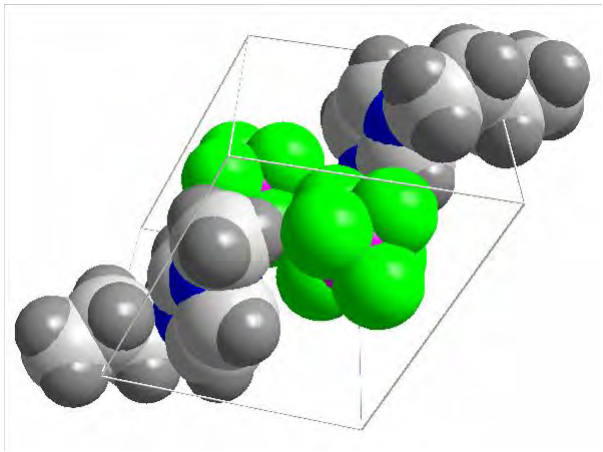
=> $Cl^- < [PF_6]^- <$ „[Teflon]$^-$“

or

$0.035 < 0.100 < 0.750\ nm^3$

$[Al(OC(CF_3)_3)_4]^-$





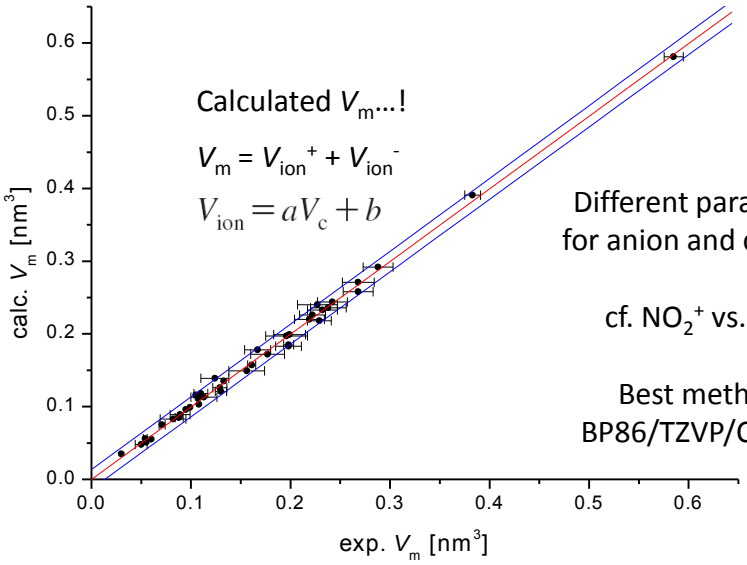
$$V_m = \frac{V_{cell}}{Z} = V_m^+ + V_m^-$$

Ion partioning according to: H.D.B. Jenkins *et al.*, *Inorg. Chem.* **1999**, *38*, 3609.

X-ray Data => Unit Cell Volume V_{cell} => Division by Z => V_m…!

Molecular Volume V_m…!

Molecular Volume V_m: calc. vs. exp.



U. P. R. M. Preiss, J. M. Slattery, I. Krossing, *Ind. Eng. Chem. Res.* **2009**, 48, 2290.

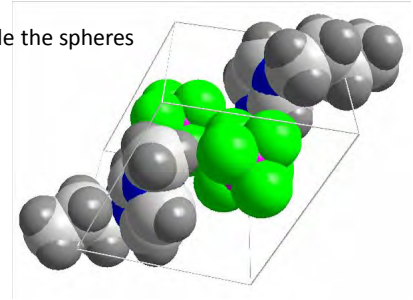
Volume Relations for Ionic Liquids

Error bars tabulated Ion Volumes: $V_m([C_4MIM][BF_4])$ = 269±30 Å^3

Resolution: Van der Waals Volumes

- calc void option of Platon[1],[2]
- assumption of fused spheres with fixed radii (here Bondi van der Waals radii)
- calculation of V_{vdw} by counting grid points inside the spheres
- packing index P (in %) as output

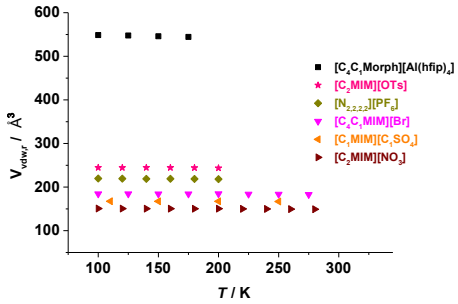
$$V_{vdw,r} = \frac{V_{cell} \cdot P}{Z \cdot 100}$$



Temperature Dependence…?

[1] A.L.Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2005
[2] P. van der Sluis and A. L. Spek, *Acta Crystallographica Section A*, 1990, **46**, 194.

T-dependence of $V_{vdw,r}$



Compounds	T / K	$V_{vdw,r}$ / Å^3
$[C_2MIM][NO_3]$	100–RT	150±1
$[C_2MIM][OTs]$	100–200	244±0
$[C_4C_1MIM][Br]$	100–275	184±1
$[C_1MIM][C_1SO_4]$	9–RT	167±1
$[C_1MIM][PF_6]$	113–293	162±2
$[N_{2,2,2,2}][PF_6]$	100–200	219±1
$[C_4C_1Morph][Al(hfip)_4]$	100–175	547±1

Almost no temperature dependence of $V_{vdw,r}$…!

ChemPhysChem **2013**, *14*, 3221–3226; *PCCP* **2013**, *15*, 8821–8830; *Angew. Chem. Int. Ed. Engl.* **2014**, *53*, 3143–3146; *Z. Anorg. Allg. Chem.* **2013**, *639*, 2153-2161.

Ion volume partitioning

$$V_{vdw,r} = V^{+}_{vdw,r} + V^{-}_{vdw,r}$$

Fixed volumes of halides based on r_{vdw}(Bondi)[1] and fixed volumes of $[BF_4]^-$, $[PF_6]^-$, $[OTf]^-$ and $[NTf_2]^-$ via a triangulation approach.

> 17 cation volumes were derived

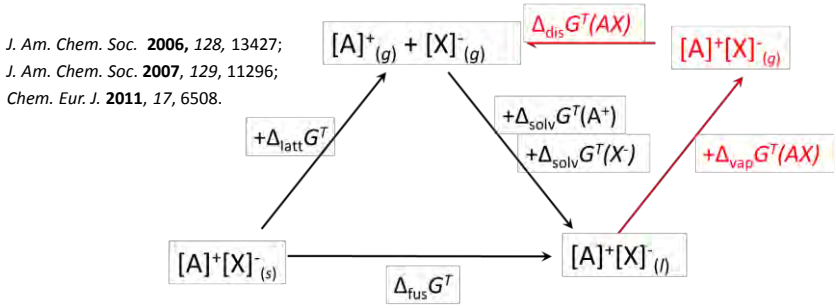
> Only one crystal structure is sufficient for the consistent calculation of $V_{vdw,r}^{+/-}$

> In agreement with exp. Charge Density Determination of IL.

[1] A. Bondi, *J. Phys. Chem.* **1954**, *58*, 929.

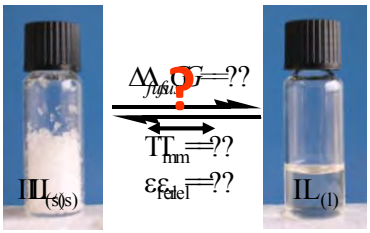
Ion	$V_{vdw,r}^{+/-}$/Å^3	No. of compounds/crystal structures
$[BF_4]^-$	50±1.2	4/5
$[PF_6]^-$	69±0.3	16/27
$[OTf]^-$	80±0.2	8/9
$[NTf_2]^-$	**147±0.7**	**41/41**
$[C_2MIM]^+$	110±1.4	7/13
$[C_4MIM]^+$	142±1.5	6/13
$[C_2C_1MIM]^+$	126±0	1/1
$[C_4C_1MIM]^+$	157±0.8	4/15
$[C_2C_1Pyrr]^+$	124±0.7	1/1
$[C_4C_1Pyrr]^+$	158±0.7	1/1
$[C_4Py]^+$	137±0	1/1
$[N_{2,2,2,2}]^+$	149±2.5	3/9
$[N_{4,4,4,4}]^+$	276±1.6	2/5

ChemPhysChem **2013**, *14*, 3221–3226 ; *Angew. Chem. Int. Ed. Engl.* **2014**, *53*, 3143–3146.



MELTING POINT PREDICTIONS

On the usefulness of the molecular Volume V_m and Radius r_m



Basic Thermodynamics of Melting

$\Delta G = \Delta H - T\Delta S$

=> *at the exp. M.P.:* $\Delta G = 0$

$$T_{\text{fus}} = \frac{\Delta_{\text{fus}} H}{\Delta_{\text{fus}} S}$$

A. Jain, S. H. Yalkowsky, *J. Pharm. Sci.* 2006, *95*, 2562.
L. Zhao, S. H. Yalkowsky, *Ind. Eng. Chem. Res.* 1999, *38*, 3581.
R.-M. Dannenfelser, S. H. Yalkowsky, *Ind. Eng. Chem. Res.* 1996, *35*, 1483.

Melting Entropy $\Delta_{fus}S$

- $\Delta_{fus}S = a \cdot \log \sigma + b \cdot \tau + c$

  σ = number of possible equal orientations in the crystal

$$\sigma = \sqrt{\sigma^{+}\sigma^{-}}$$

  σ is a symmetry number, only rotational axis C_n or S_n but no mirror planes are counted; usually σ represents the index n of the highest C_n or S_n axis.

- τ = number of torsion angles that lead to a new conformation.

J. Phys. Chem. B **2010**, *114*, 11113-11140.

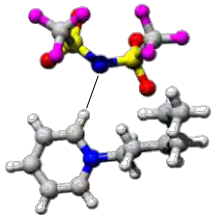
Melting Enthalpy $\Delta_{fus}H$

- $\Delta_{fus}H$ was approximated as a function of the molecular volume:

$\Delta_{fus}H = F(V_m)$ or $F(r_m)$ $\quad r_m = r_m^{+} + r_m^{-}$ $\quad r_m^{\pm} = \sqrt[3]{\frac{3V_{ion}^{\pm}}{4\pi}}$

- Neglects directed interactions, i.e.:

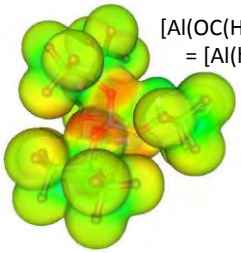
N-H in $[C_6Py][NTf_2]$: 242.3 pm



J. Phys. Chem. B **2010**, *114*, 11113-11140.

Test Set I

$$T_{fus} / K = \frac{c \cdot r_m^3}{a \cdot \ln \sigma + b \cdot \tau + 1}$$



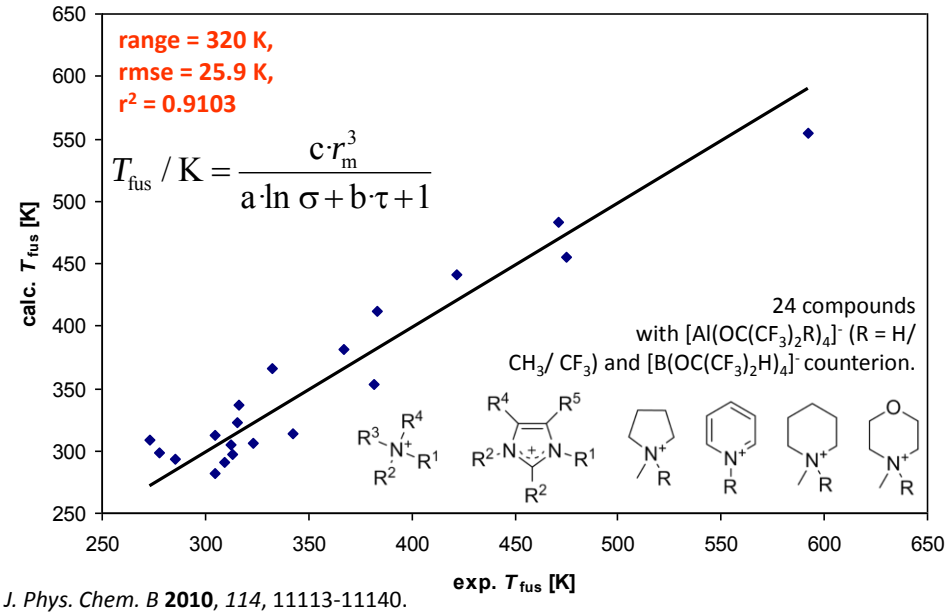
$[Al(OC(H)(CF_3)_2)_4]^-$ = $[Al(hfip)_4]^-$

Electrostatic Potential Map of $[Al(hfip)_4]^-$; our Workhorse since **1999**!

- M.P.'s of 24 model compounds with $[Al(OC(CF_3)_2R)_4]^-$ (R = H/ CH_3/ CF_3) and $[B(OC(CF_3)_2H)_4]^-$ counterion.
- **Reason:** quasi-isotropicity and very weak coordination ability make the far ordering in the lattice of their salts comparable

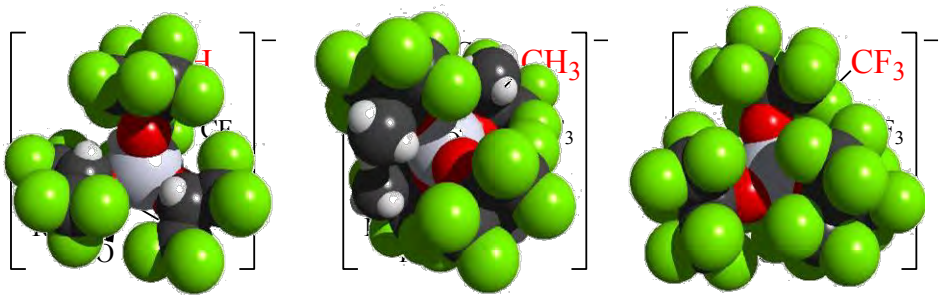
J. Phys. Chem. B **2010**, *114*, 11113-11140.

Results Test Set I



J. Phys. Chem. B **2010**, *114*, 11113-11140.

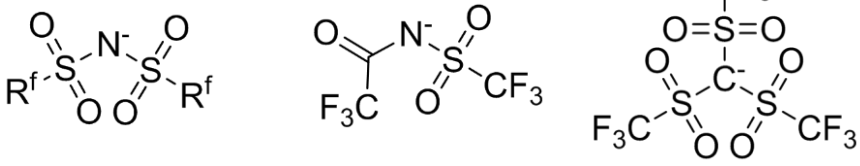
Similarities and Differences: NEt_4^+ Salts…



M.P.:	56 °C	111 °C	308 °C
V_{anion}:	0.581 nm³	0.658 nm³	0.736 nm³
σ:	4	4	4
τ:	**7**	**7**	**3**
μ_{XRD}:	0.5 – 3.7 D		

Extension to different Anions and Cations:

Formula also true for other sets with varying anions:



- larger deviations => different conformations…!
- unaccounted for as of now.

$$T_{fus} / \mathrm{K} = \frac{c \cdot r_m^3}{a \cdot \ln \sigma + b \cdot \tau + 1}$$

Nevertheless:

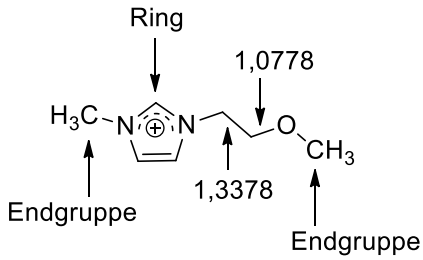
=> united set of 67 ILs (including aluminates/borates plus 10 different anions, 39 different cations, range(T_{fus}) = 337 °C)
=> Formula yields **average error** of **36.4 °C, r^2 = 0.6746**

J. Phys. Chem. B **2010**, *114*, 11113-11140.

Automated model for τ

$\tau = \Sigma(1{,}5 - 0{,}5 \cdot BO_{max}(i))$

i = skeletal atom (without rings);
BO_{max} = highest PABOON-bond order at this atom



- Skeletal atoms are 2 C- and 1 O-atom; the highest bond orders to the neighboring atoms are given.
- To consider: 2x 1,3378 and 1x 1,0778 for BO_{max}
- → τ = 2,6233

ChemPhysChem **2011**, *12*, 2959-2972.

Automated Protocol tested for 520 Salts

520 very different organic 1:1-Salts; M.P.-range: 341 °C.

$$T_{fus} = \frac{b_1 \cdot V_m + b_2 \cdot \hat{S} + b_3 \cdot \Delta_{solv} H^{\infty}}{a_1 \cdot \ln\sigma + a_2 \cdot \tau + 1}$$

$err_{ø}$ = 36.1 °C

Inclusion of directed interactions by COSMO-RS:

$$T_{fus} = \frac{b_1 \cdot V_m + b_2 \cdot \hat{S} + b_3 \cdot \Delta_{solv} H^{\infty} + b_4 \cdot H^0_{HB} + b_5 \cdot H^0_{MF} + b_6 \cdot TS^0_g}{a_1 \cdot \ln\sigma + a_2 \cdot \tau + a_3 \cdot \alpha + 1}$$

ChemPhysChem **2011**, *12*, 2959-2972.

$err_{ø}$ = 33.5 °C

Is Universal Melting Point Prediction Possible…?

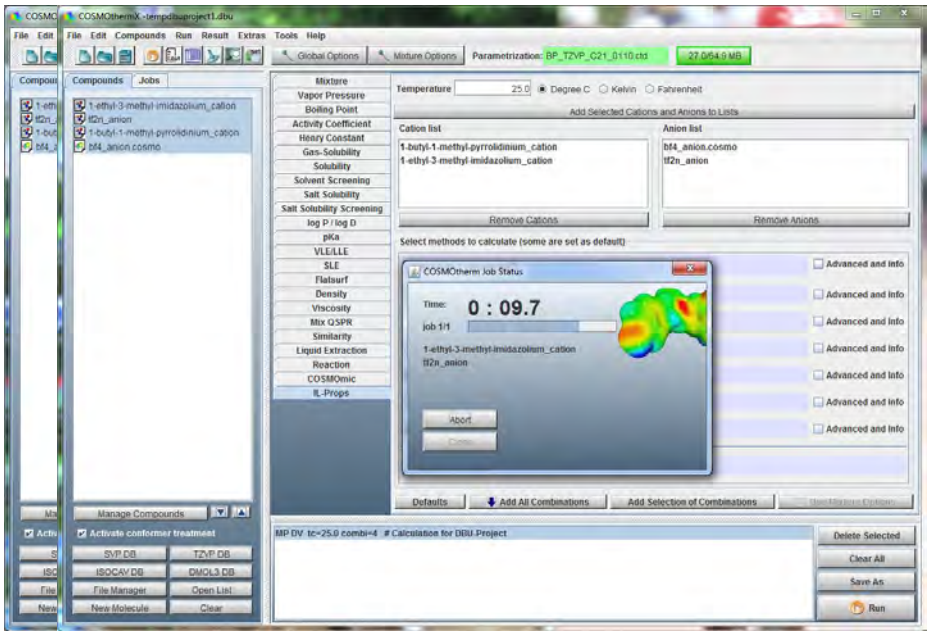
Addresses:

- Contamination
- Phase Behavior
- Liquid Crystals
- Plastic Crystals
- Pressure
- Disorder
- Defects
- Decomposition
- DSC Calibration
- Thermal History

…and automated thermodynamic Melting Point Prediction….!

ChemPhysChem **2011**, *12*, 2959 – 2972.

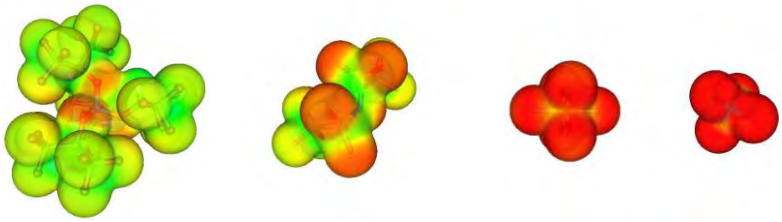
Cosmotherm, IL-Prop-Module



$[Al(hfip)_4]^-$ (hfip = $C(H)(CF_3)_2$)

0.581 nm³

$[B(hfip)_4]^-$ 0.535 nm³ | $[NTf_2]^-$ 0.220 nm³ | $[PF_6]^-$ 0.104 nm³ | $[BF_4]^-$ 0.072 nm³

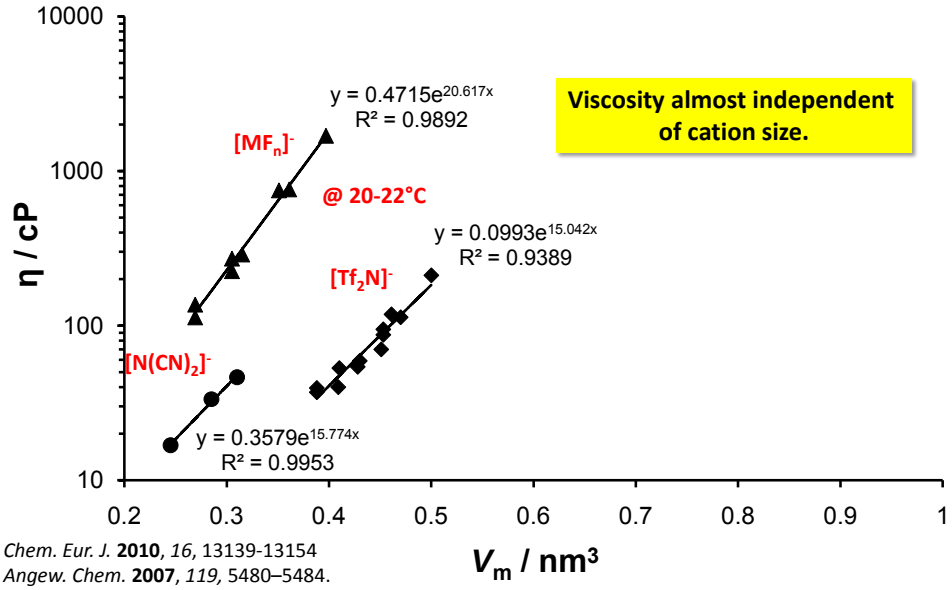


How does the size and nature of an IL-Ion influence the IL-Properties…?

Ion Size vs. Physical Properties

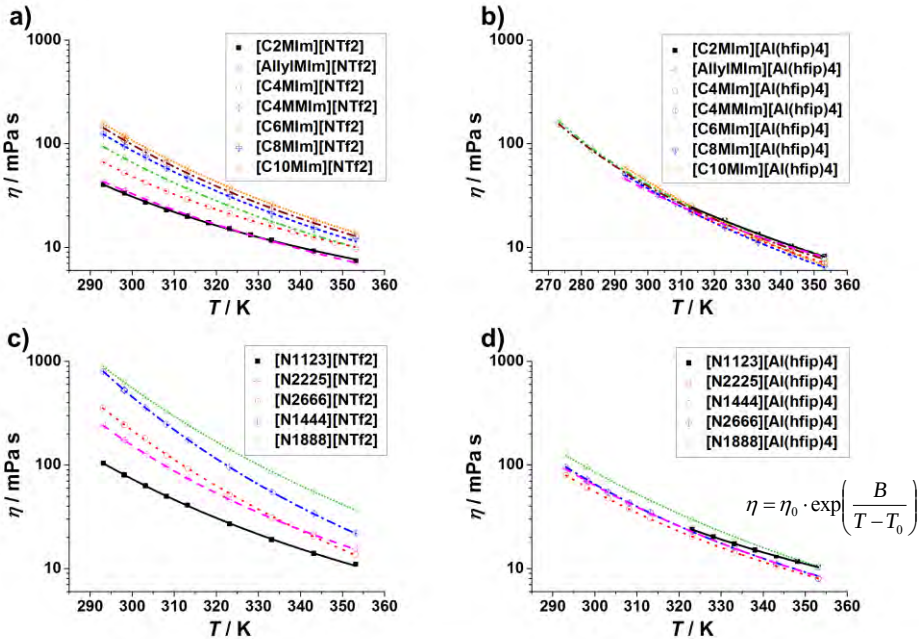
Chem. Eur. J. **2009**, 15, 1966-1976; *Chem. Eur. J.* **2010**, *16*, 13139-13154;
ChemPhysChem **2011**, *12*, DOI: 10.1002/cphc.201100214; *Dalton Trans.* **2011**, 1448-1452;
ChemPhysChem **2012**, *13*, 1802-1805; *Chem. Eur. J.* **2014**, *20*, DOI: 10.1002/chem.201400168.

Viscosities vs. Molecular Volume

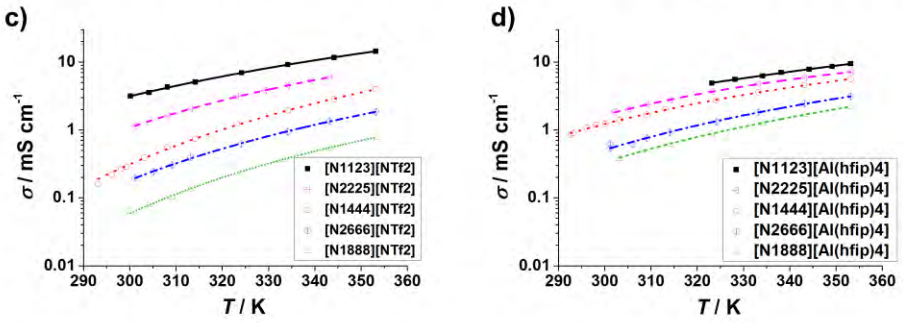


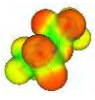
Chem. Eur. J. **2010**, *16*, 13139-13154
Angew. Chem. **2007**, *119*, 5480–5484.

Comparing the Viscosities: $[NTf_2]^-$ vs. $[Al(hfip)_4]^-$ ILs



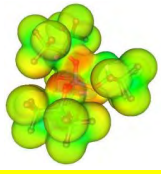
Inspecting the Conductivities: Why are the $[Al(hfip)_4]^-$ ILs so well conducting?





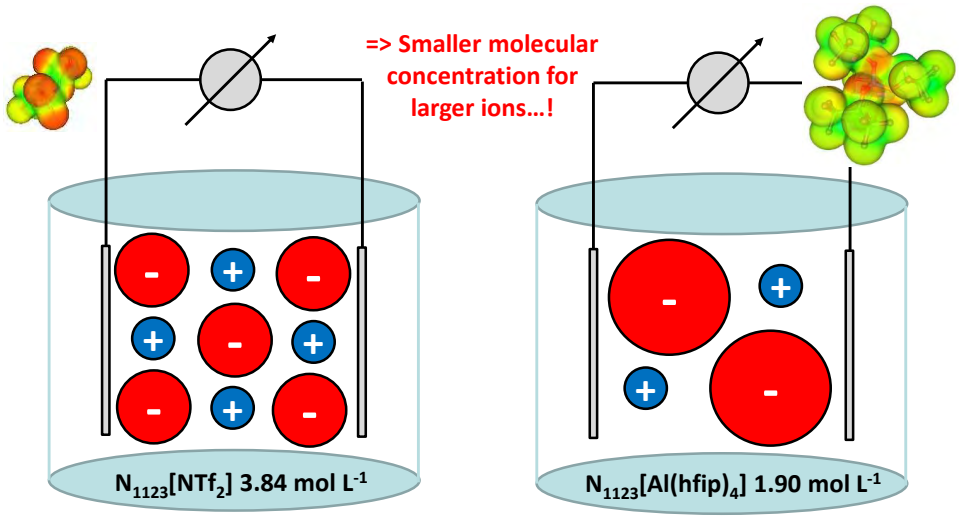
$[Al(hfip)_4]^-$ is 2.5 times as large as $[NTf_2]^-$…!

But similar conductivity…!



Volume $[NTf_2]^-$: 0.230 nm³ **Volume $[Al(hfip)_4]^-$: 0.581 nm³**

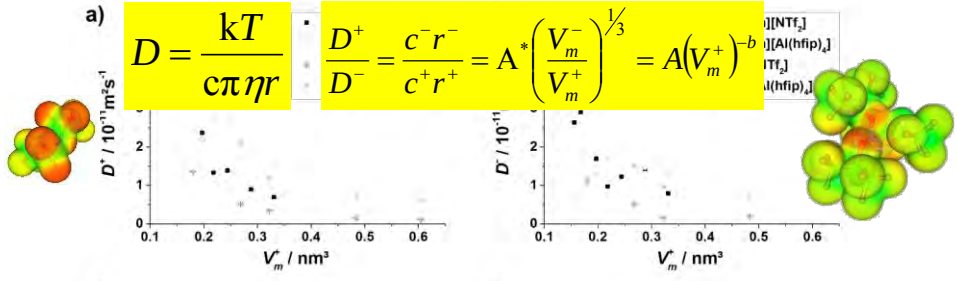
Inspecting the Conductivities: Why are the $[Al(hfip)_4]^-$ ILs so well conducting?



Volume $[NTf_2]^-$: 0.230 nm³ **Volume $[Al(hfip)_4]^-$: 0.581 nm³**

Results – Diffusion NMR-Measurements

$$D = \frac{kT}{c\pi\eta r} \qquad \frac{D^+}{D^-} = \frac{c^- r^-}{c^+ r^+} = A^* \left(\frac{V_m^-}{V_m^+}\right)^{1/3} = A\left(V_m^+\right)^{-b}$$



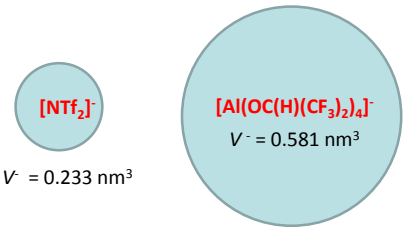
Volume $[NTf_2]^-$: 0.230 nm³ **Volume $[Al(hfip)_4]^-$: 0.581 nm³**

Ionicities: $I = \sigma_{exp}/\sigma_{calc}$

σ_{exp} = measured with conductometer.

Stokes-Einstein-Equation:

$$\sigma_{calc} = \frac{q^+ \cdot q^- \cdot \rho \cdot N_A}{M \cdot k_B \cdot T}\left(D^+ + D^-\right)$$

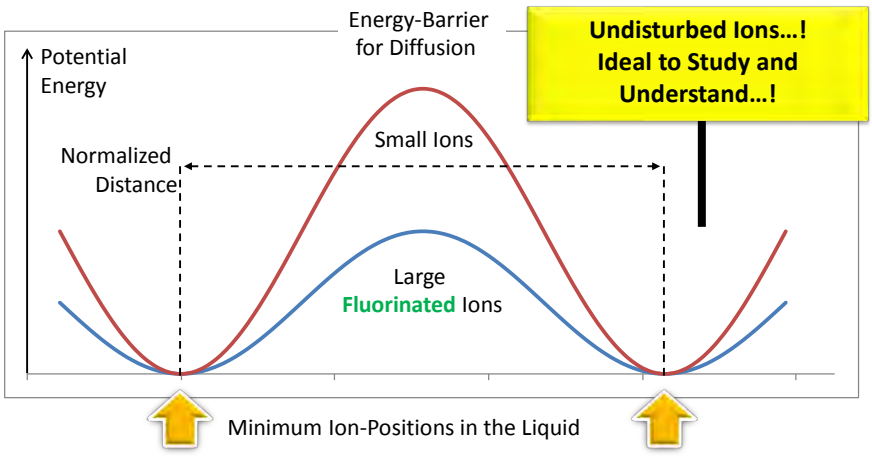


	I(NTf_2^-)	I($[Al(hfip)_4]^-$)
$[C_2MIm]^+$	0.67 (0.75)[a]	(2.10)
$[AllylMIm]^+$	0.62	**1.01**
$[C_4MIm]^+$	0.56 (0.61)[a]	**1.03**
$[C_4MMIm]^+$	0.66	**0.83**
$[C_6MIm]^+$	0.63 (0.57)[a]	0.73
$[C_8MIm]^+$	0.48 (0.54)[a]	0.82
$[C_{10}MIm]^+$	0.55	0.79
$[N_{1123}]^+$	0.82	No D^+, D^-
$[N_{2225}]^+$	-	0.69
$[N_{1444}]^+$	0.50	0.87
$[N_{1888}]^+$	No D^-	0.47
$[N_{2666}]^+$	0.74	0.80

[a] K. Ueno, H. Tokuda, M. Watanabe, *Phys. Chem. Chem. Phys.* **2010**, *12*, 1649

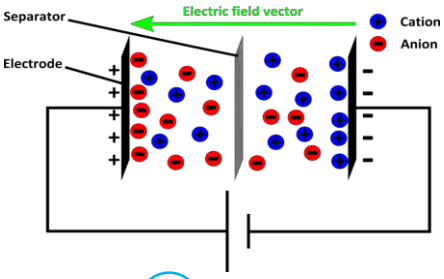
Chem. Eur. J. **2014**, *20*, 9794-9804.

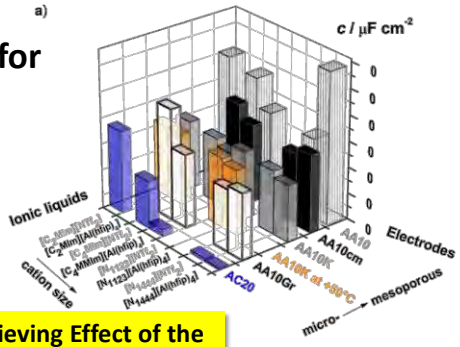
Energy Barrier for Ion Diffusion…



Chem. Eur. J. **2014**, *20*, 9794-9804.

$[Al(hfip)_4]^-$ ILs as Electrolytes for EDLC Supercapacitors





Sieving Effect of the Electrode Material…!

$$E_{max} = \frac{C \cdot U_{max}^2}{2}$$

$$P_{max} = \frac{U_{max}^2}{4 \cdot R_{eq}}$$

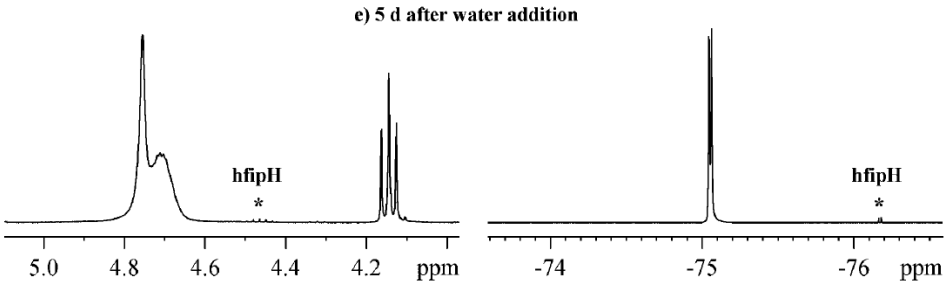
ILs: U_{max} > 5 V!!!

H_2O: 1.2 V (kinetically untill 2 V)
Organic: 2.7 to max. 4 V

With: Fraunhofer ICT, Dr. Jens Tübke
in press with *ChemElectroChem* **2015**

Changing ‘Al‘ for ‘B‘ in $[M(OR^F)_4]^-$

=> Al-O more polar than B-O…!

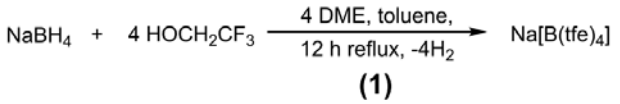


After 5 days exposure to water, slight hydrolysis (< 1 %)…

$[C_nMIM]^+$ [a] $[C_nMMIM]^+$ [c] $[C_4MMorph]^+$ [d]
$[AllylMIM]^+$ [b]

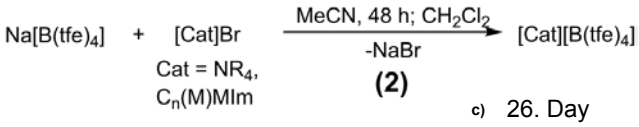
Dalton Trans. **2011**, *40*, 8114–8124.

Changing ‘Al‘ for ‘B‘ in $[M(OR^F)_4]^-$



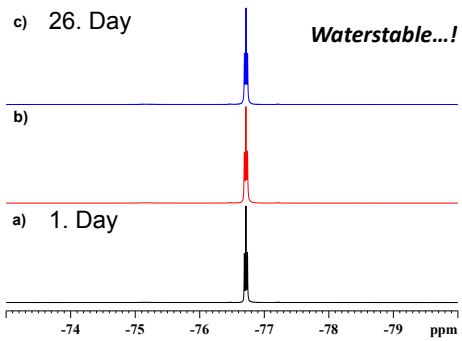
(1)

tfe = O-CH_2-CF_3



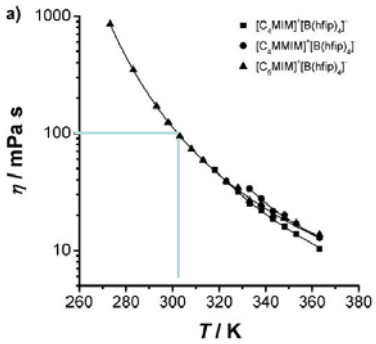
(2)

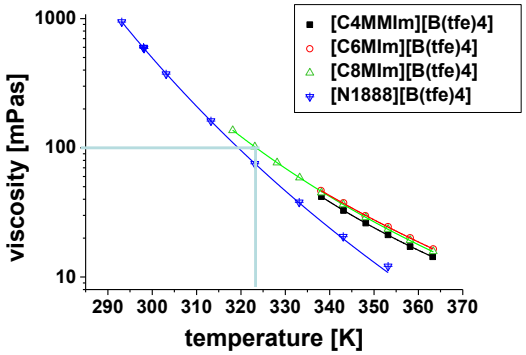
What about the Physical Properties…?



ChemPhysChem **2014**, *15*, 3729-3731.

Comparison of Viscosities #1

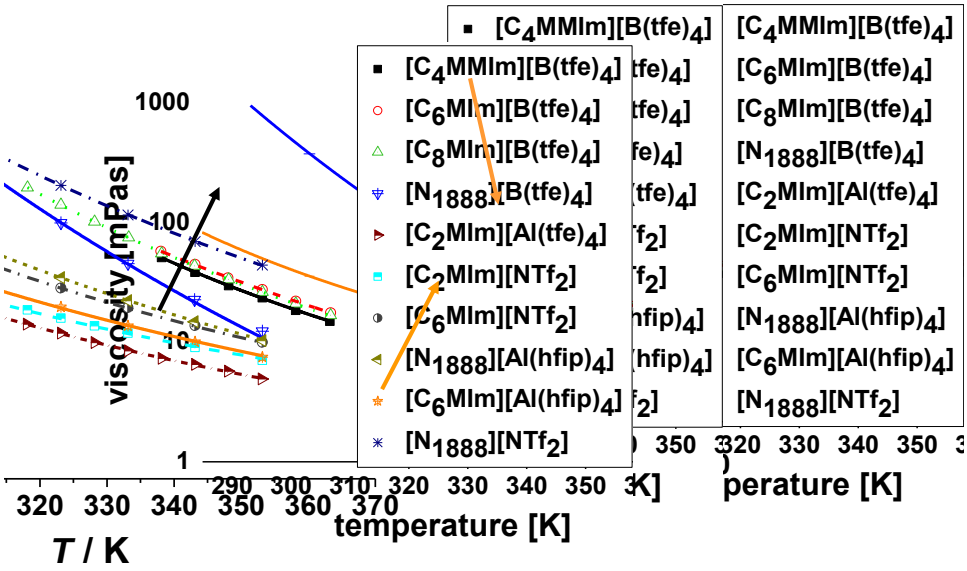




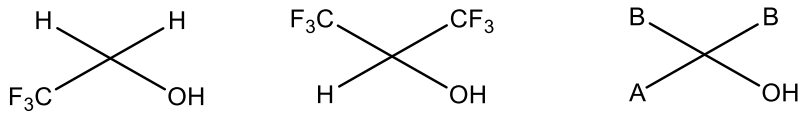
$[B(tfe)_4]^-$-ILs significantly more viscous than $[B(hfip)_4]^-$-ILs, yet clearly follow a VFT trend…!

$[B(tfe)_4]^-$-ILs reach a similar viscosity at 20 K more elevated temperatures than $[B(hfip)_4]^-$-ILs…!

Comparison of Viscosities #2



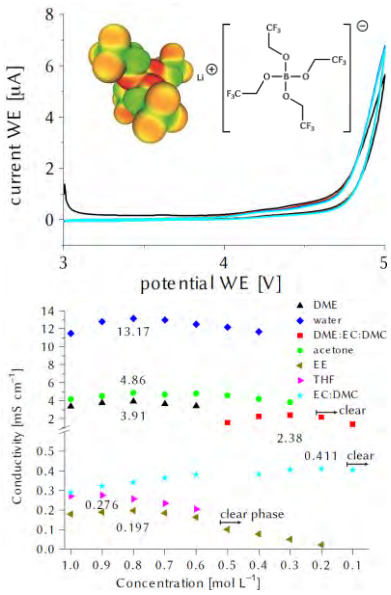
Comparison of Melting Points

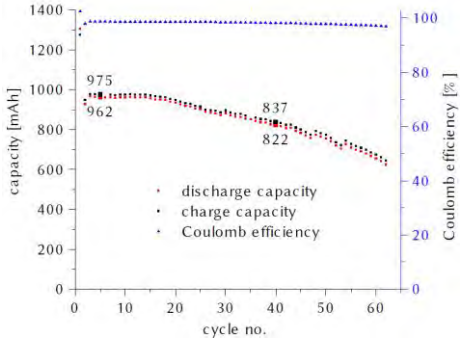


Melting Points from DSC Measurements:

Cation	$[C_4MMIm]^+$	$[C_6MIm]^+$	$[C_8MIm]^+$	$[N_{2225}]^+$	$[N_{1888}]^+$	M, R^F
mp./°C	58	45	28	89	4	B, tfe
mp./°C	68	< 0	-	-	-	B, hfip
mp./°C	< 0	5	< 0	< 0	< 0	Al, hfip

$Li[B(OTfe)_4]$ for LiB/LiSB





=> Capacity after the 40th cycle: **86 %**.
=> Analogously built LiSB with electrolyte DME/DOL (1 : 1) and 8 wt.-% $Li[NTf_2]$: Capacity after 40 cycles: only **70 %**.

=> Improvement…!

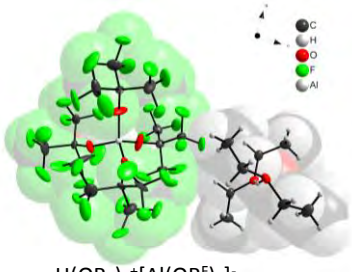
ChemPhysChem **2014**, in press.

Can we Establish pH Scales for ILs …?

Barrhorn, CH

Brønsted Acidity in Ionic Liquids…!

Brønsted Acidity and Aluminates…?

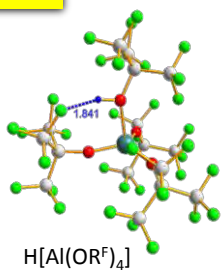


$H(OR_2)_2^+[Al(OR^F)_4]^-$;
$OR_2 = OMe_2, OEt_2$, THF

Eur. J. Inorg. Chem, **2005**, 1979-1989.

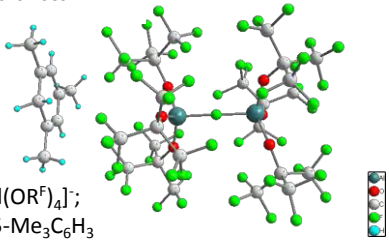
Brønsted Acidity in non polar organic solvents…!

$R^F = C(CF_3)_3$



$H[Al(OR^F)_4]$

Organometallics **2012**, *31*, 7485-7491.
DOI: 10.1021/om300776a.



$H(Mes)^+[Al(OR^F)_4]^-$;
$Mes = 1,3,5\text{-}Me_3C_6H_3$

Andi Reisinger,
Anne Kraft,
Daniel Himmel

Why is $H(OEt_2)_2^+[Al(OR^F)_4]^-$ such a good Initiator for Isobutene Polymerisation…?

Kat [mg]	T_{start}	ΔT	t	yield [g]	M_n	M_w	M_w/M_n	α in %
30	-60	**60**	1s	11,7	12211	63407	**4,3977**	n.b.
20	-51	**72**	1s	11,7	10094	55896	**5,5374**	n.b.
10	-50	**65**	1s	11,6	13923	66518	**4,7777**	n.b.
5	-50	**64**	1s	12,3	12025	64045	**5,326**	n.b.

$C(CH_3)_3^+$ as Intermediate…!

≈ 100 % within 1 second…!

= 4 µmol => for comparison: typical load of normal initiator =250-500 µmol…!

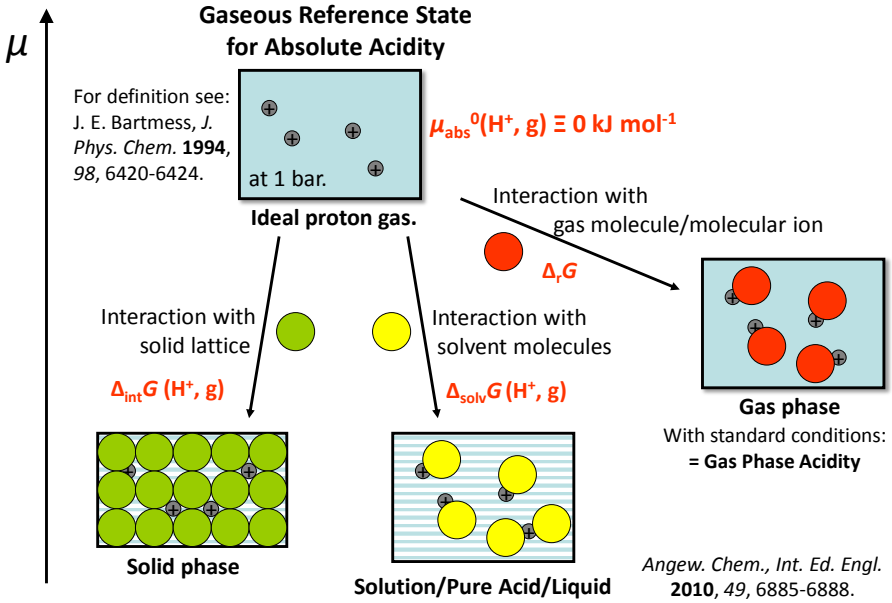
=> Also very high α-selectivity (≈ 95 %)

$$H(OEt_2)_2^+ + H_2C{=}C(CH_3)_2 \xrightarrow{\text{Gas phase}} C(CH_3)_3^+ + 2\ OEt_2$$

$\Delta_r G° = +107$ kJ mol^{-1} (MP2/def2-QZVPP)

Four Patents with BASF AG, 2006-2010.

A Unified Brønsted Acidity scale…!



Angew. Chem., Int. Ed. Engl. **2010**, *49*, 6885-6888.

Acidity in The Liquid Phase: pH Scales

$$HA_{(solv)} \overset{\text{Solvent}}{\rightleftharpoons} H^+_{(solv)} + A^-_{(solv)}$$

pH value: pH = -log(*a*(H⁺, solv.))

For ΔpH = Δ*a*(H⁺) = 1 holds: R*T* ln Δ*a*(H⁺) = 2.303 R*T* log(10)
= **5.71 kJ mol⁻¹** at *T* = 298.15K.

Scales: => Specific for each solvent (Water, AN, DMSO, …)

=> Use pK_a-value and activities to assess pH value for comparison of acidity in **one medium**.

Using the Anchor Points: Definition of non-standard potentials and absolute pH_{abs}

$$\mu_{abs}(H^+, solv) = \Delta_{solv}G^0(H^+) - pH \cdot 5.71\ kJ\ mol^{-1}$$

Anchor point

Assessing pH: Using experimental or calculated pK_a-values

pH for weak acids HB:	pH = ½(pK_a –lg(a($B^-_{solv.}$)),
Medium strong acids:	pH = –log(–K_a/2 + (K_a^2/4 + K_a*c_0/1M)$^{1/2}$
Strong acids HB:	pH =–lg(a($B^-_{solv.}$))

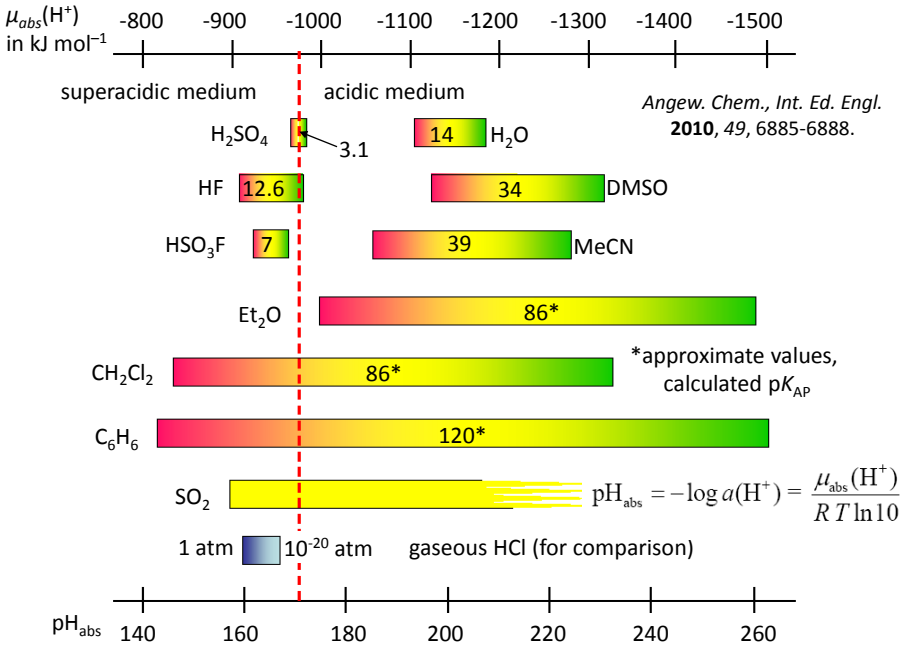
$$pH_{abs} = \frac{\mu_{abs}(H^+_{(solv)})}{-5.71\ kJ\ mol^{-1}}$$

Anchor Points: Standard Gibbs Solvation Energies of the Proton

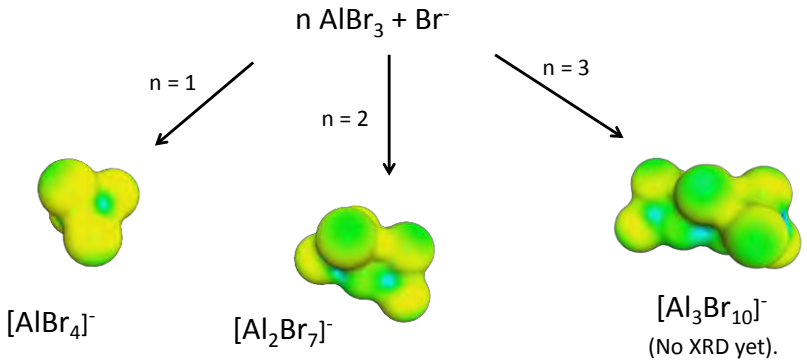
$\mu_{abs}^0(H^+) = \Delta_{solv}G^0(H^+, g \rightarrow solv)$ (in kJ mol^{-1})			
NH_3(fl.)	-1202	Pyridine	-1133
NMP	-1130	DMSO	-1124
DMF	-1119	**Water**	**-1105**
1-BuOH	-1101	**EMIMBr**	**-1101**
EG	-1101	PG	-1099
1-PrOH	-1096	MeOH	-1094
EtOH	-1093	$PhNO_2$	-1071
HMPT	-1065	MeCN	-1058
PC	-1055	$MeNO_2$	-1010
Et_2O	-998	Sulfuric acid	-966
HCl, gas 10^{-3} bar	***-930***	Fluorosulfuric acid	-924
hydrogen fluoride	-908	Sulfur dioxide	-898
dichloromethane	-834	Benzene	-816

Chem. Eur. J. **2014**, *20*, 4194–4211. (**VIP-paper**)

Absolute Protochemical Windows



How acidic can you get with $HBr/AlBr_3$…?



- Cf. Gaseous $AlBr_3$ is a Lewis Superacid (FIA 505 kJ mol^{-1}).
- Bromoaluminates are **Pearson-soft** anions and should **destabilize proton coordination**.
- Cf. D. Farcasiu, S. L. Fisk, M. T. Melchior, K. D. Rose, *J. Org. Chem.* **1982**, *47*, 453 for an NMR study showing similar acidity to HF/SbF_5.

FIA(AlX_3) in Gaseous and Solid Phase

$$MX_3 + F^- \rightarrow F\text{-}MX_3^- \quad -\Delta H = ?$$

FIA	MX_3 (g)	AlX_3 (s)	Δ(g-s)
$AlCl_3$	502	376	126
$AlBr_3$	505	404	101
AlI_3	(535)	429	106
$GaCl_3$	429	-	-
$GaBr_3$	426	-	-
GaI_3	(457)	-	-

Calc. @ ccsd(t)/DZ→QZ//MP2/QZVPP

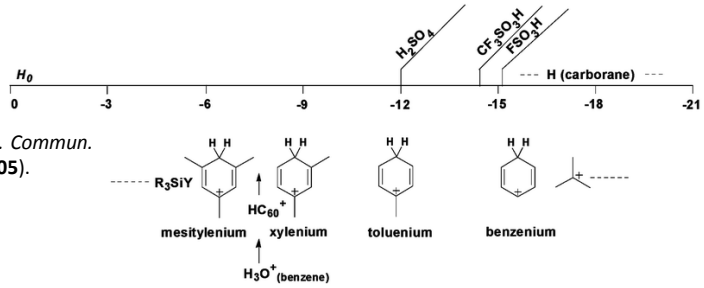
Solid $AlBr_3$ and AlI_3 are clearly stronger Lewis acids.

=> F(C.N.): Sublimation enthalpies for X = Br, I lower than for X = Cl

How acidic can you get with $HBr/AlBr_3$…?

Limiting Factor: Solvents / Media

=> **Case Studies:** simple Carbocations



Reed, C. *Chem. Commun.* 1669-1677 (**2005**).

Chem. Eur. J. **2015**, in press, *ChemPhysChem* **2015**, in press.

How acidic can you get with $HBr/AlBr_3$…?

Increasing Acidity

Medium…	$\mu_{abs}(H^+)$**	pH_{abs}
C_6MIMBr *	**-1159**	**203**
H_2O *	-1145	201
$BMIMAlCl_4$*	**-1132**	**198**
$BMIMAlBr_4$ *	**-1127**	**197**
0.1 M HBr/C_6MIMBr	**-1119**	**196**
1 M HCl/H_2O	-1105	194
0.1 M $AlCl_3$ + 0.1M $HCl/C_6MIMAlCl_4$	**-984**	**172**
H_2SO_4 *	-975	171
0.1 M $AlBr_3$ + 0.1M $HBr/C_6MIMAlBr_4$	**-974**	**171**
0.1 M $tBu[FSO_3]$ (from tBu-OH in HSO_3F)	-963	169
0.1 M $AlBr_3$ + 0.1M HBr /$C_6MIMAl_2Br_7$	**-958**	**168**
HF*	-944	165
0.1 M $AlBr_3$ + 0.1M HBr /$C_6MIMAl_3Br_{10}$	**-938**	**164**
1 M SbF_5/HF	-908	159

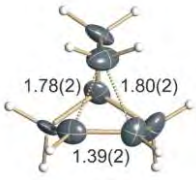
* pH from autoprotolysis; ** in kJ mol^{-1}.

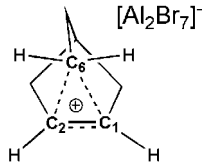
Compound calculations, rCCC model, Error bar 10 to 15 kJ mol^{-1}

Chem. Eur. J. **2015**, in press, *ChemPhysChem* **2015**, in press.

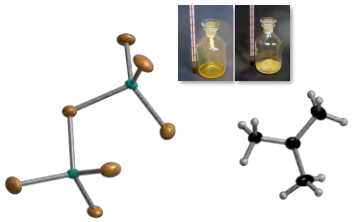
Daniel Himmel

How acidic can you get with $HBr/AlBr_3$…?

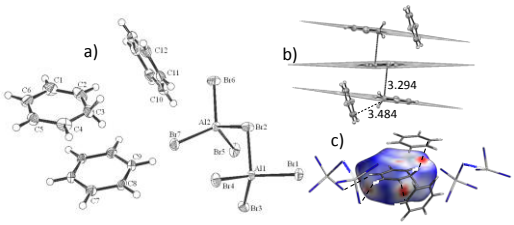




Science **2013**, *341*, 62-64.



Chem. Eur. J. **2013**, *19*, 109-116.



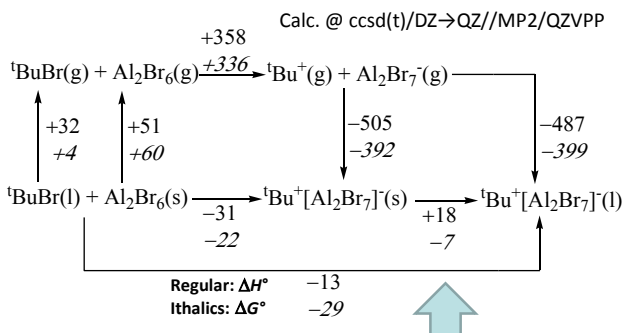
Angew. Chem. **2014**, *126*, 1715-1718.

⇒ High Acidities reached,
⇒ Should be used more frequently…!

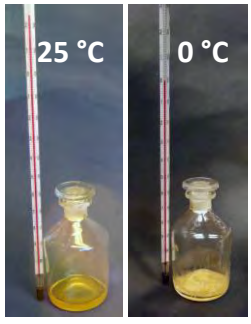
⇒ **But:** How acidic…?

A Superacidic Ionic Liquid…!

Formation and Thermodynamics



In fine agreement with the experimental m.p. of 2 °C…!



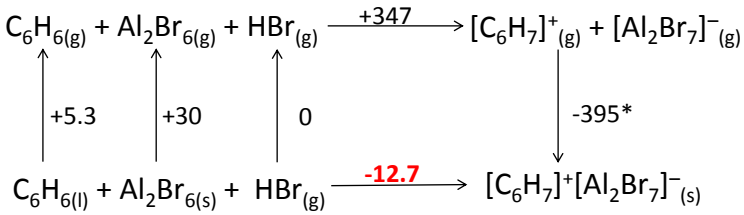
$pH_{abs}(C(CH_3)_3^+(Al_2Br_7)^-,l)$ = **171**
Cf.
$pH_{abs}(C(CH_3)_3^+$ in $HSO_3F)$ = **168**

Chem. Eur. J. **2013**, *19*, 109-116.

F. Scholz, 2010-13

Energetics Protonated Benzene from $AlBr_3$/HBr

Standard Gibbs Energies throughout:



$pH_{abs}(H(C_6H_6)^+[Al_2Br_7]^-,l)$ = **163**
Cf.
$pH_{abs}(H(C_6H_6)^+$ in $HF/SbF_5)$ = **156**

HBr	+1331.8 →	H^+ + HBr	NIST
$C_6H_6 + H^+$	-725.4 →	$[C_6H_7]^+$	NIST
$Al_2Br_6 + Br^-$	-259.2 →	$[Al_2Br_7]^-$	ccsd(t)/DZ→QZ//MP2/QZVPP

Angew. Chem. Int. Ed. Engl. **2014**, online available.
DOI: 10.1002/ange.201308120.

* U. Preiss, S. P. Verevkin, T. Koslowski, I. Krossing, *Chem. Eur. J.* **2011**, *17*, 6508-6517.
U. Preiss, V. N. Emel'yanenko, S. P. Verevkin, D. Himmel, Y. U. Paulechka, I. Krossing, *ChemPhysChem* **2010**, *11*, 3425-3431.

Acid / Cation	Medium: HSAB-Hard vs. HSAB-Soft	pH_{abs}
$C(CH_3)_3^+$	0.1 M in HSO_3F	**168**
	$[C(CH_3)_3]^+[Al_2Br_7]^-$ neat liquid	**171**
$H(Mesitylene)^+$	0.1 M in Difluorobenzene ($[Al(OR^F)_4]^-$ Anion)	**164**
	0.1 M in SO_2 ($[Al(OR^F)_4]^-$ Anion)	**164**
	0.1 M in $[BMP][Al_2Br_7]$	**170**
	0.1 M in $[BMP][Al_3Br_{10}]$	**169**
$H(Benzene)^+$	100 % Protonation in HF/SbF_5	**156**
	0.1 M in $HBr/AlBr_3$ melt	**163**

Advanced Grant 2012-2017

2D-Plot of Absolute Electrochemical and Protochemical Potentials

THE PROTOELECTRIC POTENTIAL MAP

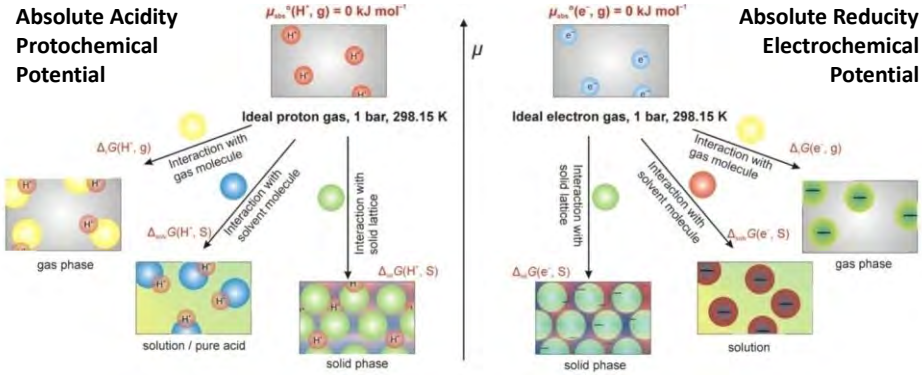
Angew. Chem., Int. Ed. Engl. **2010**, *49*, 6885-6888.
Chem. Eur. J. **2011**, *17*, 5808-5826 (**VIP-paper**).
Chem. Eur. J. **2012**, *18, 9333-9340.*
Chem. Eur. J. **2014**, *20*, 4194-4211(**VIP-paper**).

Definition of Reference States

Chemical Potential Scales to Compare Acid Base and/or Redox Reactions over Medium and Phase Boundaries.

For definition of ideal H^+ and e^- gas see: J. E. Bartmess, *J. Phys. Chem.* **1994**, *98*, 6420-6424.

Absolute Acidity Protochemical Potential



Absolute Reducity Electrochemical Potential

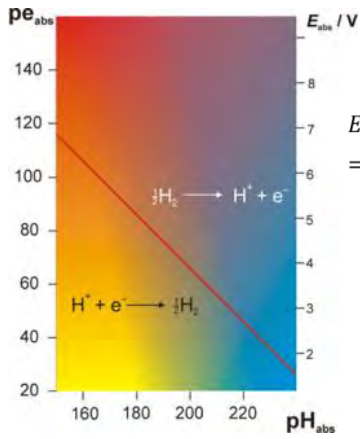
Angew. Chem., Int. Ed. Engl. **2010**, *49*, 6885-6888.
Chem. Eur. J. **2011**, *17*, 5808-5826 (**VIP-paper**).
Chem. Eur. J. **2012**, *18*, 9333-9340.

Chem. Eur. J. **2014**, *20*, 4194-4211(**VIP-paper**).

The Alliance of pH_{abs} and pe_{abs}

$$pe_{abs} = -\frac{\mu_{abs}(e^-)}{RT\ln 10}$$

$$pe = -\lg a(e^-)$$



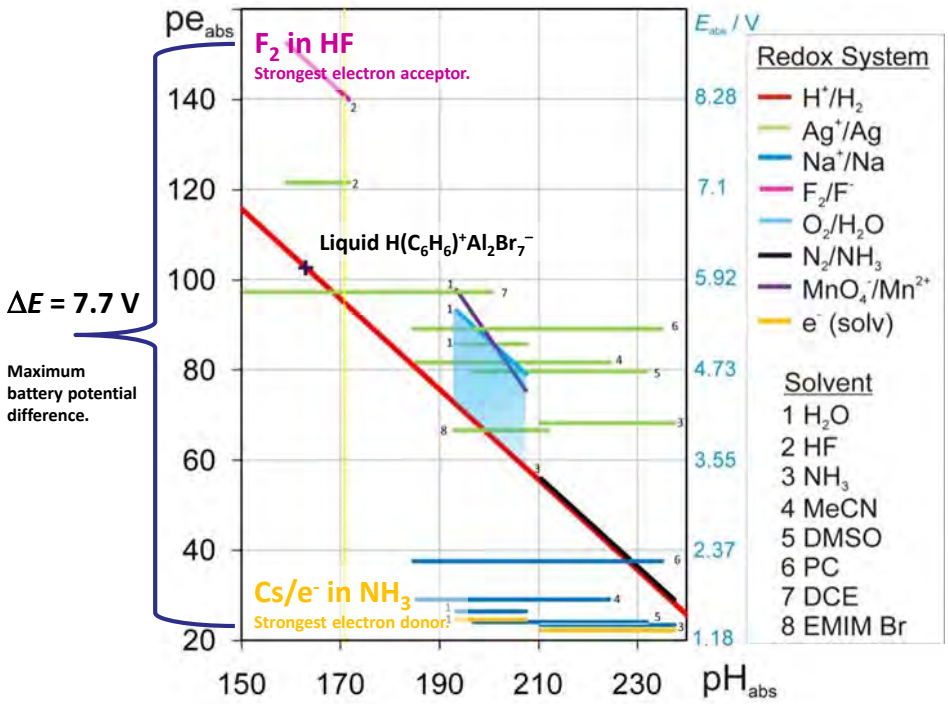
$$E_{abs} = \frac{-\mu_{abs}(e^-)}{F} = \frac{RT\ln 10}{F} \cdot pe_{abs} = 0.05916\,V \cdot pe_{abs}$$

Chem. Eur. J. **2014**, *20*, 4194-4211 (**VIP-paper**).

$$pH = -\lg a(H^+)$$

$$pH_{abs} = -\frac{\mu_{abs}(H^+)}{RT\ln 10}$$

$$\mu_{abs}(H^+, solv) = \Delta_{solv}G°(H^+) - pH \cdot RT\ln 10$$



Advanced Grant 2012-2017

General Setup - Experimental Realization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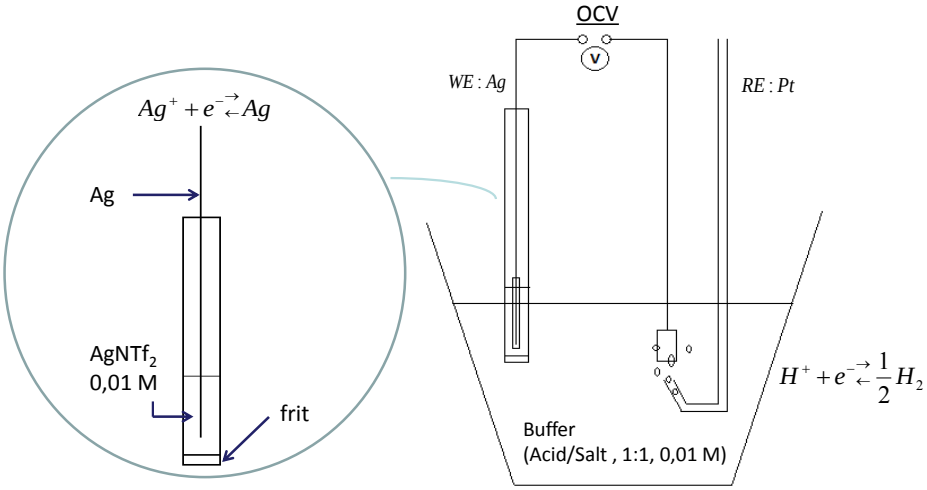
2012 - 2015

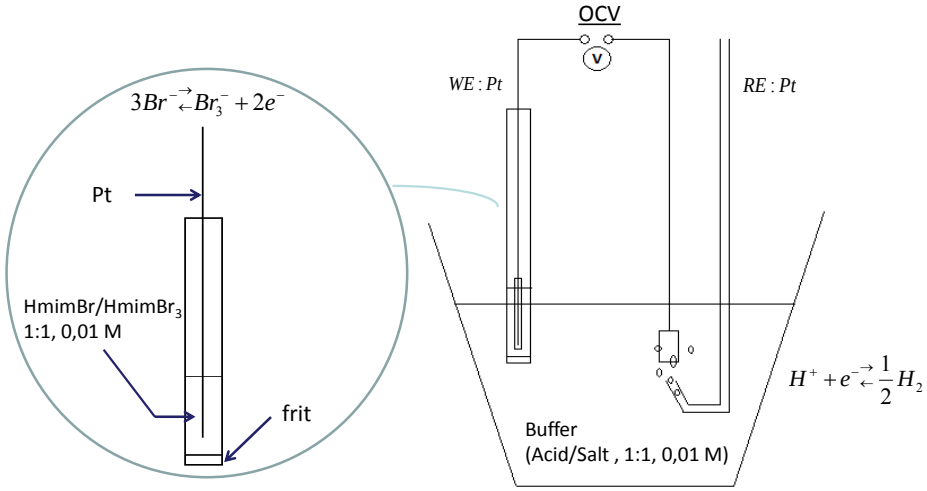
Determination of Redoxpotentials_E vs. RE
OCV (Open Circuit Voltage)_ Both Half Cells in Equilibrium

$$Ag\left|Ag^{+}\right\|H^{+},H_2\left|Pt\right.$$

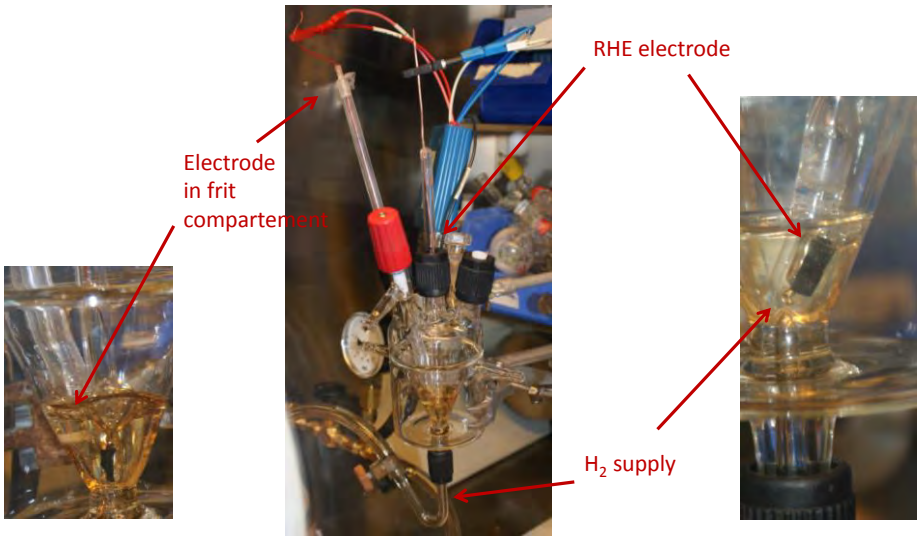


Determination of Redoxpotentials_E vs. RE
OCV (Open Circuit Voltage)_ Both Half Cells in Equilibrium

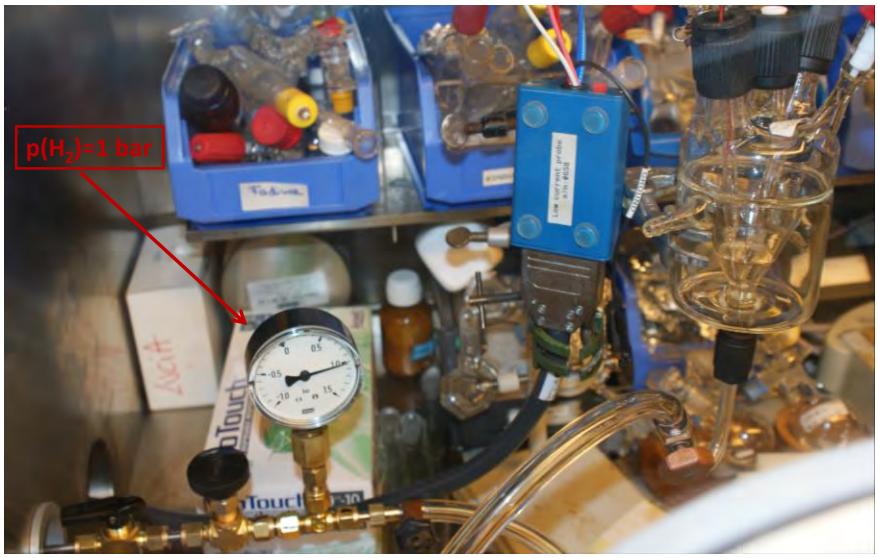
$$Pt\left|Br_3^-, Br^-\right\vdots H^+, H_2\left|Pt\right.$$



Experimental Setup in Argon Glove Box

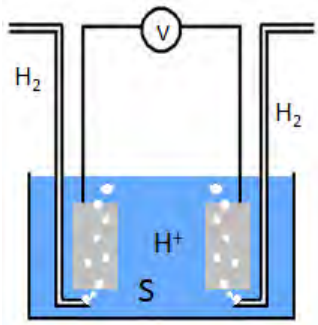


Experimental Setup in Argon Glove box

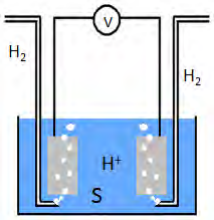


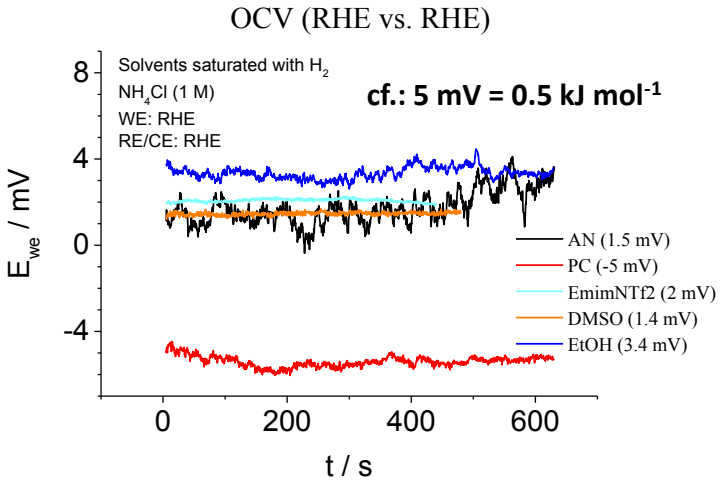
RHE in Non-Aqueous Solvents:

- Acetonitrile (AN)
- Propylene Carbonate (PC)
- $EmimNTf_2$
- DMSO
- Ethanol (EtOH)



Reversible Hydrogen Electrode (RHE) in Non-Aqueous Solvents





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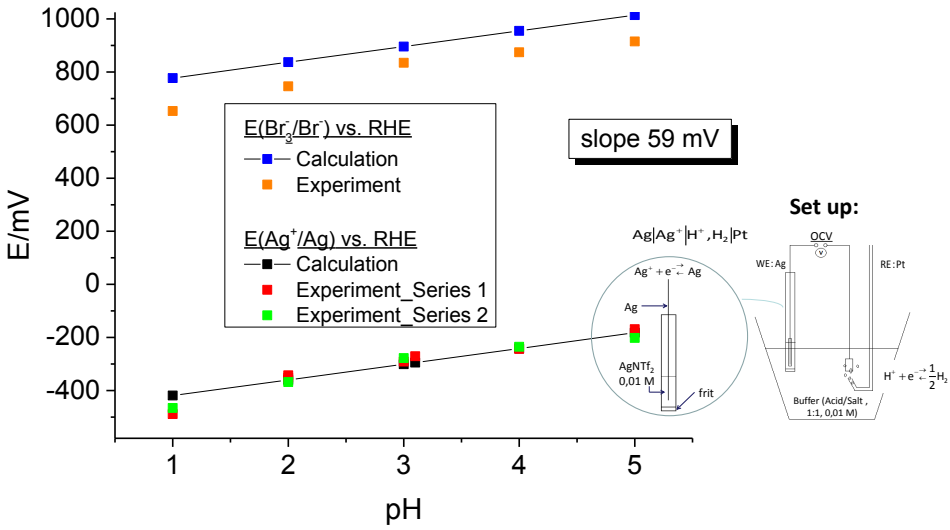
RHE in [Hmim]Br

Establishment of Different Reference Systems in [Hmim]Br: RHE, Ag^+/Ag and Br_3^-/Br^-



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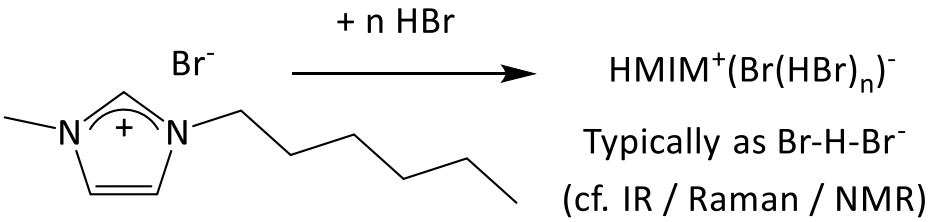
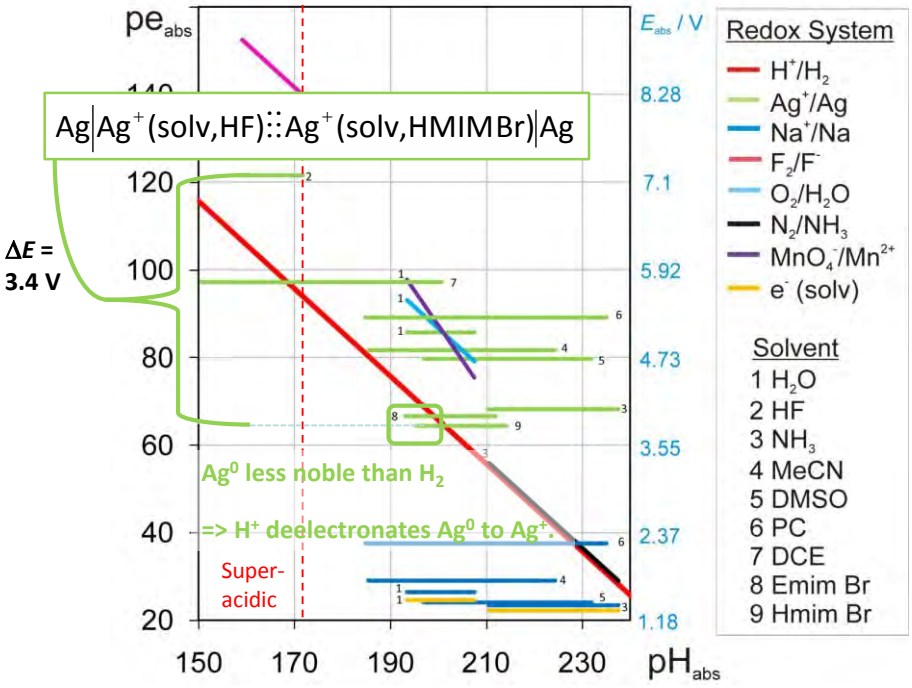
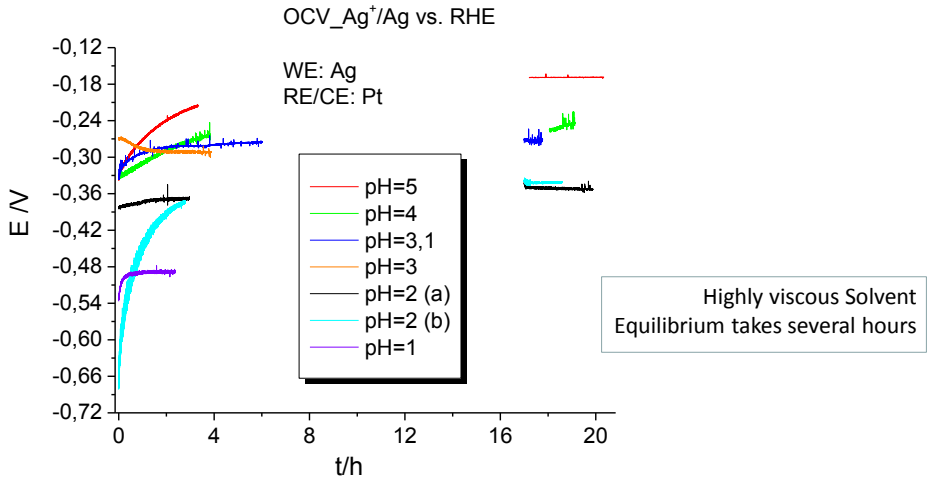
Ag in Acidic [Hmim]Br

Is Ag a Noble Metal in this Medium….?





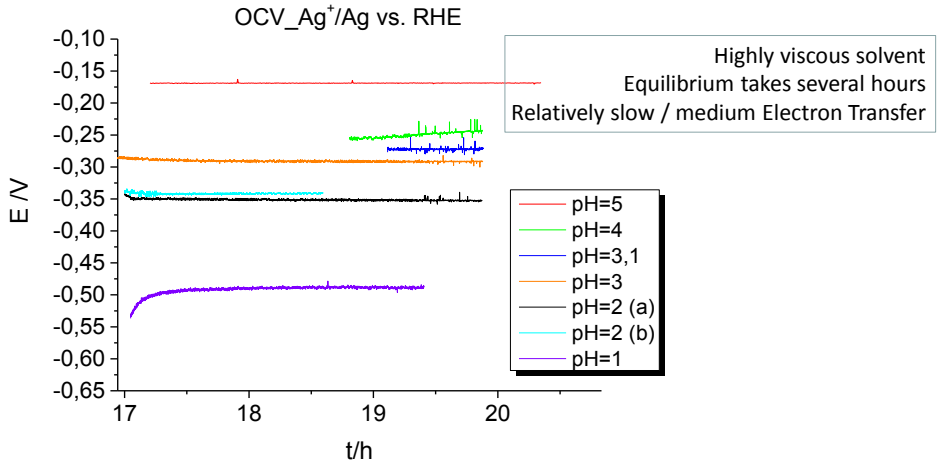
E(Ag⁺/Ag) vs. RHE* in [Hmim]Br at Different pH Values



c(AgPf)=0,01 mol/l
Variation of pH value via HBr concentration

*RHE (Reversible Hydrogen Electrode)

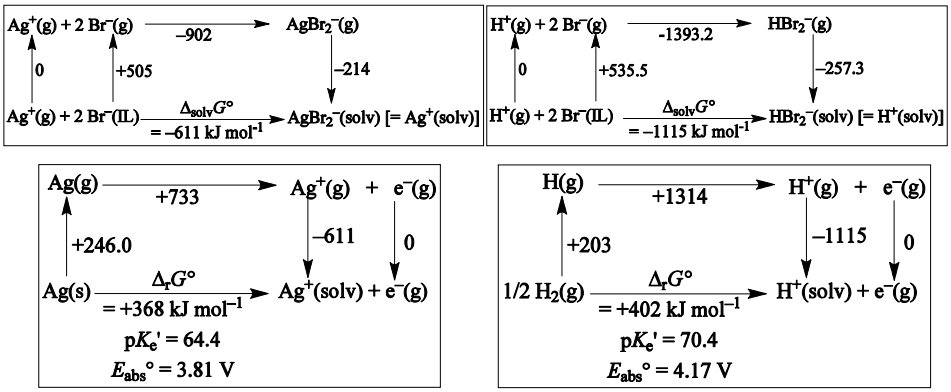
E(Ag⁺/Ag) vs. RHE* in [Hmim]Br at Different pH Values



AgPf 0.01 mol/l
Variation of pH value via HBr concentration

*RHE (Reversible Hydrogen Electrode)

QM_BFHC_Ag⁺/Ag and H⁺/H₂ in [Hmim]Br at Standard Conditions



Nernst:

$\Delta E = \Delta E_{abs}^{\circ} + \frac{RT}{zF} \ln a(Ag^+) + 59\ \text{mV} \cdot \text{pH}$

$\Delta E = -478\ \text{mV} + 59\ \text{mV} \cdot \text{pH}$

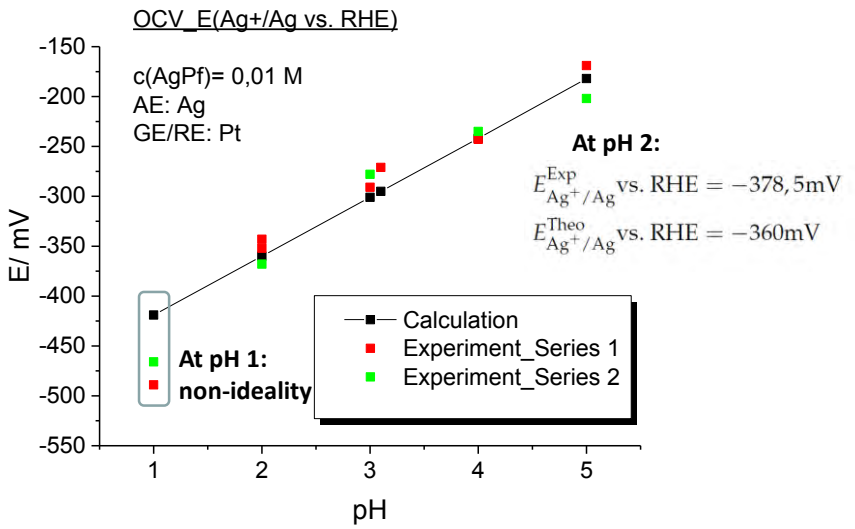
$E_{abs}^{\circ}(Ag^+/Ag) = 3.81\ \text{V}$

$c(Ag^+) = 0.01\ \text{M}$

$E_{abs}^{\circ}(H^+/H_2) = 4.17\ \text{V}$

pH: variation c(HBr)

E(Ag⁺/Ag) vs. RHE in [Hmim]Br at Different pH Values



Dissolution of Silver in Acidic [Hmim]Br

$$Ag^0_{solid} + 2[Hmim]Br + H^+_{solv} \rightarrow [AgBr_2]^-[Hmim]^+ + 0.5H_2 + [Hmim]^+$$

Addition of water ⟶ $AgBr\downarrow$, dissolution with KCN for AAS

		AAS [ppm]	Weight [mg]	Visual Inspection
Ag-Flake	Solution 1 **pH=0, 32 days**	-	0,51 (whole flake)	dissolved completely
	Solution 2 **pH=0.5, 19 days**	128	0,87 (whole flake)	dissolved completely
Ag-Wire	Solution 1 **pH=0, 32 days**	-	15,03	affected
	Solution 2 **pH=0.5, 19 days**	747	4,76	affected
	Solution 3 **pure HmimBr, > 6 month**	<0,5	-	unchanged

WCAs…

WCA Development…
Reactive Cations…
Super Acids…
Polymerisation…
Catalysis…

AKK

…ILs

…IL Development
…MP Prediction
…Phys. Properties Prediction
…Phys. Properties Determination
…Li-Ionic Liquids

…Ionic Systems…

Thank You…!

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EPF Lausanne, Uni Freiburg, Landesstiftung Baden-Württemberg,
ERC, IoLiTec, BASF AG, MERCK, SOLVAY.
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