



# Unified pH

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## pH

- Best known parameter for expressing acidity

$$\text{pH} = -\log a(\text{H}^+, \text{solv})$$

- In every solvent (medium) the **activity of solvated proton** is linked to its **concentration** in *that solvent*

## The standard state

- The **standard state** is 1 M (or 1 m) H<sup>+</sup> in *that solvent*

The standard state is *concentration-based*

- The same concentration of solvated protons can **in different solvents have hugely different ability** to influence processes

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## Solvents differ by the ability to solvate H<sup>+</sup>

- By the ability of decreasing the **chemical potential** of H<sup>+</sup>
- Transfer free energies of H<sup>+</sup> from water to solvents:

Solvent	$\Delta G^\circ_{\text{transfer}}$ of H <sup>+</sup> from H <sub>2</sub> O (kJ/mol)
MeNO <sub>2</sub>	95
MeCN	46.4
MeOH	10.4
Water	0.0
DMSO	-19.4
Pyridine	-28

- One pH unit corresponds to 5.7 kJ/mol

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## As a Result ...

- The same pH in different solvents refers to different acidity in terms of chemical potential
  - And it is the chemical potential that matters (catalysis, acidic hydrolysis, redox potential, ...)

**Example:**  
 pH 7 in water is neutral,  
 pH 7 in MeCN is strongly acidic

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## Absolute pH?

- Proposal: proton gas at 1 bar as reference state ( $\text{pH}_{\text{abs}} = 0$ )
- Definition via chemical potential:

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



Angewandte Chemie

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### A Unified pH Scale for All Phases\*\*

Daniel Himmel, Sascha K. Goll, Ivo Leitte, and Ingo Krossing\*

Arrhenius,<sup>[1]</sup> Brønsted,<sup>[2]</sup> and Lowry<sup>[3]</sup> defined acids as proton donors and bases as proton acceptors, a concept nowadays known as Brønsted acidity. It is used in all chemistry-related areas<sup>[4]</sup> including materials science<sup>[5]</sup> energy storage,<sup>[6]</sup> catalysis,<sup>[7-9]</sup> environmental science,<sup>[8]</sup> and molecular biology.<sup>[10]</sup> In aqueous solution Brønsted acidity is expressed quantitatively as the pH value (referred to here as "conventional pH value") that is  $-\text{lg}a(\text{H}^+, \text{aq})$  with the activity of the hydrated proton  $a(\text{H}^+, \text{aq})$  given in  $\text{mol L}^{-1}$ .<sup>[11]</sup> Within one homogeneous medium, pH differences are proportional to electrochemical potential differences and thus directly connected to thermodynamics.<sup>[12]</sup> The concept of pH [or  $-\text{lg}a(\text{H}^+, \text{solv})$ ] for nonaqueous solutions is less common, but self-consistent pH<sub>s</sub> scales of acidity and/or basicity exist in DMSO,<sup>[13]</sup> acetonitrile,<sup>[14]</sup> and other solvents. Importantly, the acidities determined in different solvents and expressed as conventional pH values in those solvents are not directly comparable.

To express the acidity of strongly acidic media—for example, pure mineral acids—the Hammett function and the  $H_0$  value<sup>[15]</sup> were developed. For aqueous solutions of strong acids, the  $H_0$  scale can be viewed as a continuation of the pH scale into the realm of negative conventional pH values. The  $H_0$  value is currently the most common parameter for quantifying the acidity of superacidic media,<sup>[16]</sup> that is, Brønsted acids stronger than 100% sulfuric acid.<sup>[16]</sup> However, although  $H_0$  values are widely used, they do not represent a "thermodynamic" acidity scale, which one should be able to validate, for example, by electrochemical measurements or computations.<sup>[17]</sup> The first proposals for a unified acidity scale, which would make it possible to quantitatively compare acidity throughout different media, date back to the 1950s.<sup>[18]</sup> Approaches to thermodynamic acidity values were developed by Immler,<sup>[19]</sup> Alexandrov,<sup>[20]</sup> and Strehlow.<sup>[21]</sup> Although correct in their essence, the approaches have not found widespread application owing to experimental difficulties.

Herein we propose a unified Brønsted acidity scale on the basis of the absolute chemical potential of the proton in any medium. In this scale we define the reference state for maximum acidity as the absolute standard chemical potential  $\mu_{\text{abs}}^{\ominus}(\text{H}^+, \text{g})$  of the proton in the gas phase which is arbitrarily set to 0 kJ mol<sup>-1</sup>. In fact, this standard state—the ideal proton gas at 1 bar and 298.15 K—is physically highly unstable, but it can be calculated very well and corresponds to the standard state of neutral gases. The acidity and hence the chemical potential of the gaseous proton  $\text{H}^+(\text{g})$  is lowered by the interaction with any type of medium, that is, by complexation of  $\text{H}^+$  with molecules in the gas phase, solution, or in the solid state (Figure 1). Solid-state acidity is not discussed in detail here, but a concept to establish a thermodynamic acidity scale for ionic solids has been developed by Maier<sup>[22]</sup> and can be included in our concept without problems.

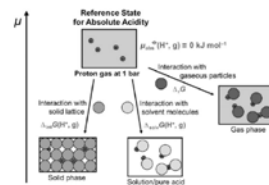
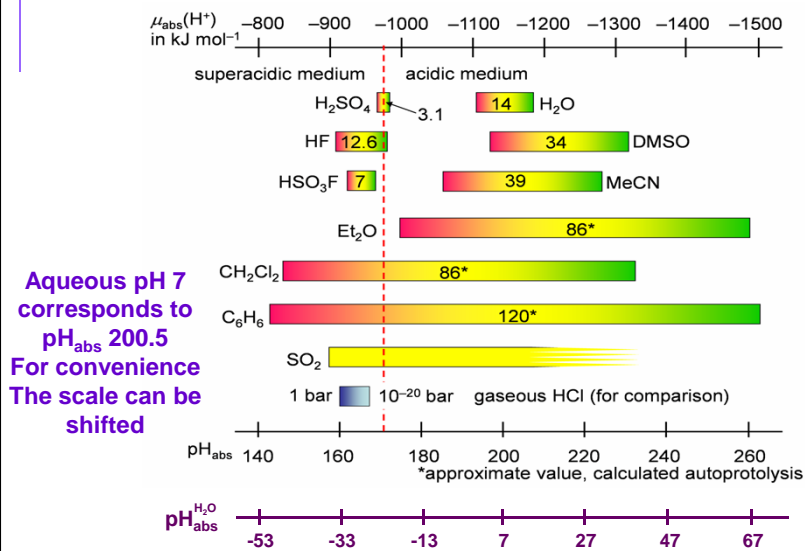


Figure 1. The reference state of maximum acidity for the unified Brønsted acidity scale and the quantitative thermodynamic relations to Brønsted acidity in all phases.

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## Acidities in solvents become comparable



D. Himmel et al *Angew. Chem. Int. Ed.* 2010, 49, 6885-6888

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The picture on the  
previous slide was  
computational

Can  $\text{pH}_{\text{abs}}$  be measured?

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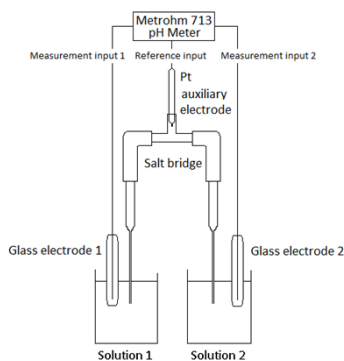
## Can $\text{pH}_{\text{abs}}$ be measured?

- Obvious technique: **potentiometry**
- Issues:
  - Standard state is not experimentally realizable, so, **measurements are relative**
    - Large resistance of the electrode system
  - When measuring between different solvents huge **Liquid Junction Potential** emerges
    - Very difficult to account for
  - **Non-polar solvents are tricky** because of low conductivity

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## First experimental realization

- $\text{H}_2\text{O}$ , MeOH, MeCN mixtures
- **Differential potentiometry** using metal-contact glass electrodes
- **LJP** estimated by the Izutsu approach



A. Suu et al *Anal. Chem.* 2015, 87, 2623-2630

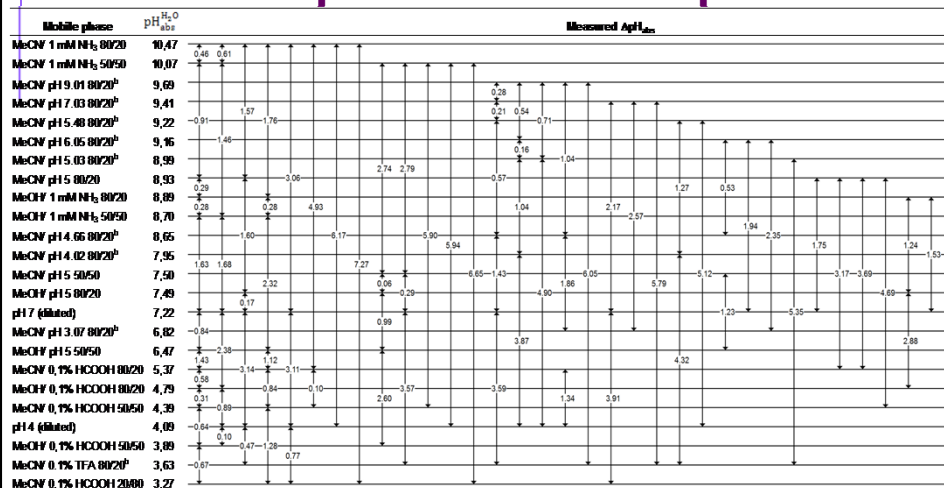
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## What are the advantages of $pH_{abs}$ ?

- **Rigorous comparison of acidities between different solvents**
  - Acidities of LC mobile phases with different solvent composition
- **Rigorous evaluation of extreme acidities**
  - Solutions of strong acids in non-aqueous solvents
- **Evaluating acidity with negligible concentration of solvated protons**
  - Evaluating the direct effect of acidity in general acid catalysis
    - Leaving aside sterics, etc

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## Absolute pH of LC mobile phases



- $pH_{abs}^{H_2O} = pH_{abs} - 193.5$  (making  $pH_{abs}$  comparable to aqueous pH)
- 83 relative measurements
- Span of the pH scale 7.25 and consistency  $s = 0.14$

A. Suu et al *Anal. Chem.* 2015, 87, 2623-2630

## Acidities of LC mobile phases

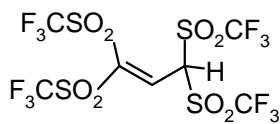
Mobile phase	pH <sub>abs</sub> <sup>H<sub>2</sub>O</sup>	w <sub>w</sub> pH
MeCN/ 1 mM NH <sub>3</sub> 80/20	10.47	9.75
MeCN/ 1 mM NH <sub>3</sub> 50/50	10.07	9.75
MeCN/ pH 5 80/20	8.93	5.00
MeOH/ 1 mM NH <sub>3</sub> 80/20	8.89	9.75
MeOH/ 1 mM NH <sub>3</sub> 50/50	8.70	9.75
MeCN/ pH 5 50/50	7.50	5.00
MeOH/ pH 5 80/20	7.49	5.00
pH 7 (diluted) <sup>b</sup>	7.22	7.16
MeOH/ pH 5 50/50	6.47	5.00
MeCN/ 0.1% HCOOH 80/20	5.37	2.68
MeOH/ 0.1% HCOOH 80/20	4.79	2.68
MeCN/ 0.1% HCOOH 50/50	4.39	2.68
pH 4 (diluted) <sup>b</sup>	4.09	4.15
MeOH/ 0.1% HCOOH 50/50	3.89	2.68

A. Suu et al *Anal. Chem.* 2015, 87, 2623-2630

## Acid catalysis in low polarity solvents

- Mukaiyama aldol, Hosomi–Sakurai, and Friedel–Crafts acylation, Nazarov cyclization, ...

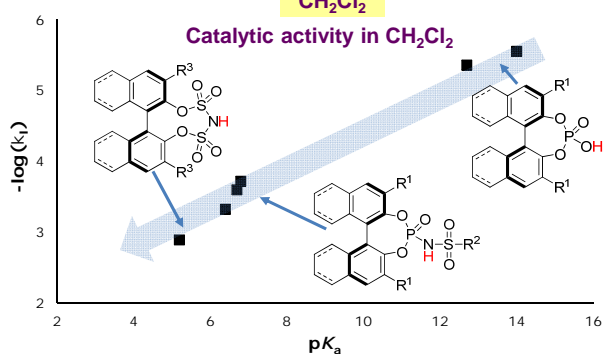
Solvents:  
C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, PhCl, CH<sub>2</sub>Cl<sub>2</sub> ...



pK<sub>a</sub> in DCE -15.4  
pK<sub>a</sub> in MeCN -2.8

D. Höfler *Angew. Chem. Int. Ed.* 2017, 56, 1411–1415

Solvents:  
CH<sub>2</sub>Cl<sub>2</sub>

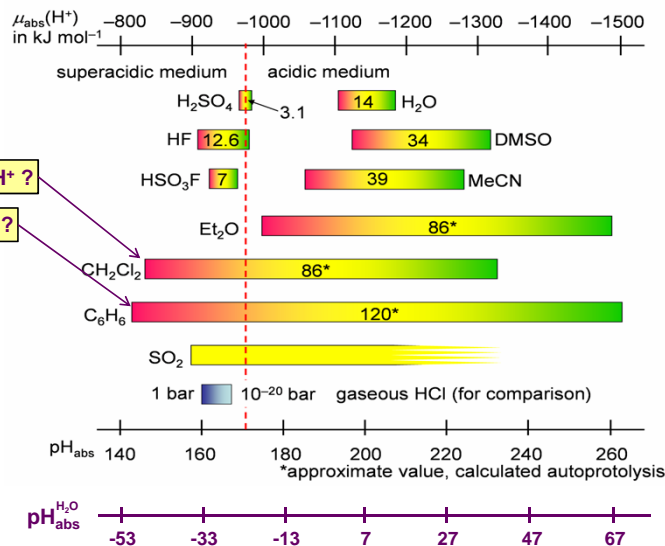


K. Kaupmees et al, *Angew. Chem. Int. Ed.* 2014, 52, 11569

To what extent are reactions governed by acidity?

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## Solvated protons in low polarity solvents?



D. Himmel et al *Angew. Chem. Int. Ed.* 2010, 49, 6885-6888

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## Acidity scale in 1,2-DCE

- $\epsilon = 10$
- Down to  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}} = -13$
- $\text{pH}_{\text{DCE}} = 30$
- Linked to the  $\text{pH}_{\text{abs}}$  scale via  $\text{Tf}_2\text{NH}$ 
  - Using high-level Computations
- There is essentially no  $\text{DCEH}^+$  in solution!
  - But can be protonated impurities

	$\text{p}K_{\text{p,r}}$	$\text{p}K_{\text{a,r}}$	$\text{p}K_{\text{a,DCE}}$	$\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$	
66	TfOH	-11.4	-11.3	33.7	-9.0
67	$\text{C}_6\text{H}_5\text{SO}(=\text{NTf})\text{NHTf}$	-11.5	-11.7	33.3	-9.4
68	$\text{TFCH}(\text{CN})_2$	-11.6	-11.5	33.5	-9.2
69	Br-TCNP	-11.8	-11.8	33.2	-9.5
70	$[\text{C}(\text{CN})_2=\text{C}(\text{CN})]_2\text{NH}$	-11.8	-12.0	33.0	-9.7
71	3,5-( $\text{CF}_3$ ) $_2$ - $\text{C}_6\text{H}_3$ -TCNP	-11.8	-12.0	33.0	-9.7
72	$\text{Tf}_2\text{NH}'$	-11.9	-12.0	33.0	-9.7
73	4-Cl- $\text{C}_6\text{H}_4\text{SO}(=\text{NTf})\text{NHTf}$	-12.1	-12.3	32.7	-10.0
74	Cl-TCNP	-12.1	-12.1	32.9	-9.8
75	$(\text{C}_3\text{F}_7\text{SO}_2)_2\text{NH}$	-12.1	-12.3	32.7	-10.0
76	$(\text{C}_4\text{F}_9\text{SO}_2)_2\text{NH}$	-12.2	-12.4	32.6	-10.1
77	CN- $\text{CH}_2$ -TCNP	-12.3	-12.4	32.6	-10.1
78	$(\text{C}_2\text{F}_5\text{SO}_2)_2\text{NH}$	-12.3	-12.4	32.6	-10.1
79	$\text{CF}_3$ -TCNP	-12.7	-12.8	32.2	-10.5
80	$\text{HClO}_4$	-13.0	-12.8	32.2	-10.5
81	$\text{CF}_2(\text{CF}_2\text{SO}_2)_2\text{NH}$	-13.1	-13.1	31.9	-10.8
82	4- $\text{NO}_2$ - $\text{C}_6\text{H}_4\text{SO}(=\text{NTf})\text{NHTf}$	-13.1	-13.3	31.7	-11.0
83	$\text{HB}(\text{CN})_4$	-13.3	-13.3	31.7	-11.0
84	$(\text{FSO}_2)_3\text{CH}$	-13.6	-13.6	31.4	-11.3
85	$\text{TF}_2\text{CH}(\text{CN})$	-14.9	-15.0	30.0	-12.7
86	2,3,4,5-tetracyanocyclopentadiene	-15.1	-15.1	29.9	-12.8
87	CN-TCNP	-15.3	-15.3	29.7	-13.0

E. Paenurk et al *Chem. Sci.* 2017, 8, 6964



## UnipHied



- **EMPIR Network**
  - European Metrology Programme for Innovation and Research
  - 17FUN09 (H2020)
- **Main aim:** to establish measurement capability of pHabs
  - Incl for routine labs
- **Partners:**
  - UT (Tartu, scientific leader), LNE (France, coordinator), BFKH (Hungary), CMI (Czech Republic), DFM (Denmark), IPQ (Portugal), PTB (Germany), SYKE (Finland), TÜBITAK-UME (Turkey), ANBSensors (United Kingdom), FCiencias.ID (Portugal), Uni Freiburg (Germany)



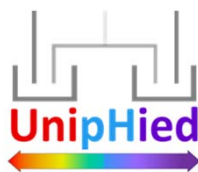
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## Thanks to all participants!

Main actors up to now:  
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Andreas Ermantraut, Jaak Nerut, Rasmus Born, Daniel  
Himmel, Ingo Krossing**

Consultants: Enn Lust, Kosuke Izutsu, Rouvim Kadis, Thorsten Koslowski



and all **UnipHied** partners!



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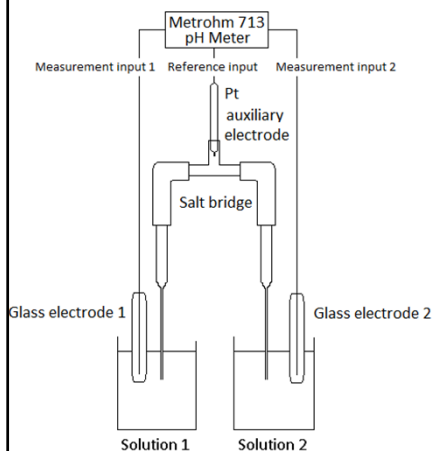
## How to measure?

### Direct experimental comparison of acidities of solutions made in different solvents

- (More or less) achieved this far:
  - Pure water vs pure acetonitrile
    - In order to compare with calculations
  - Acetonitrile solutions with different acidities
  - Acidity comparisons of LC mobile phases
    - All are aqueous-organic
  - Few more mixtures

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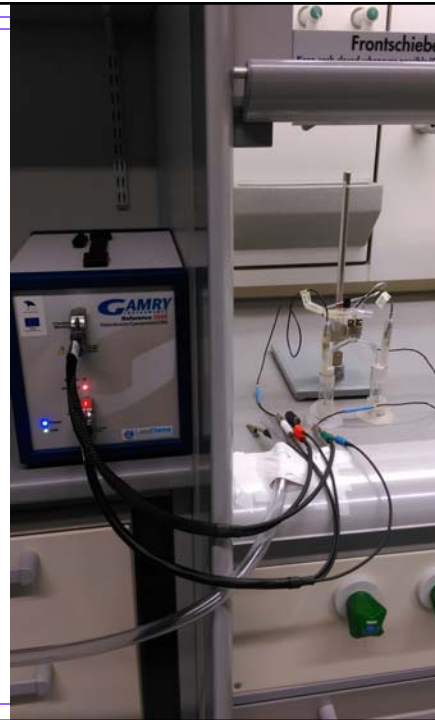
### Differential potentiometry (1) pH meter Metrohm 713 with differential input using metal-contact glass electrodes



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## Differential potentiometry (2)

- **Potentiostat** using metal-contact glass electrodes
- Some reference measurements with hydrogen electrode
  - Establishing slopes of glass electrodes



## Electrodes

- Solid-contact hand-made in St Petersburg
- Very old people, no successors, „dying art“
- **Negotiations are under way to send somebody there to learn this**

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## Cells/setup

- It is a **secondary measurement**
- Choice depends on bridge electrolyte



## Method/procedure

- Measurement solutions are connected via salt bridge
  - glass electrode is in both solutions
  - Bridge solution: ionic liquids; 0.05 M  $\text{Et}_4\text{NClO}_4$  solution in acetonitrile; no bridge solution
- After each measurement the electrodes are switched
  - then the measurement is repeated
- Average of several measurements is taken for calculations
- Gloveboxes are used if anhydrous conditions



## Calculations

$$\square \Delta E = E_{measured} + \boxed{\text{LJP}_{B\_S1} - \text{LJP}_{B\_S2}}$$

$$\bullet \Delta pH = \frac{\Delta E}{\text{average\_slope}}$$

Major headache!

- Average slope of the two electrodes is used
- Electrode slopes determined in water using standard buffer solutions or with hydrogen electrode

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## Liquid junction potential (LJP) $E_j$

- Divided into three parts:
  - $E_j(a)$  differences in ion concentrations and mobilities

$$E_j(a) = \left(-\frac{RT}{F}\right) \left[ (t_{M1} - t_{X1}) \ln \left( \frac{a_{MX2}}{a_{MX1}} + (t_{M2} - t_{M1} - t_{X2} + t_{X1}) \right) \times \left( 1 - \frac{a_{MX1}}{a_{MX2} - a_{MX1}} \ln \frac{a_{MX2}}{a_{MX1}} \right) \right]$$

- $E_j(b)$  solvation differences of ions

$$E_j(b) = \text{slope} \times \left(-\frac{1}{2F}\right) [(t_{M1} + t_{M2})\Delta G_t^0(M) - (t_{X1} + t_{X2})\Delta G_t^0(X)]$$

- $E_j(c)$  solvent-solvent interactions
  - Literature data available for some solvents

$$\mathbf{LJP} = \mathbf{E_j(a)} + \mathbf{E_j(b)} + \mathbf{E_j(c)}$$

Electrochemistry in Nonaqueous Solutions, Kosuke Izutsu, 26

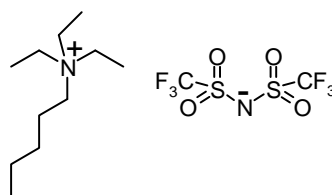
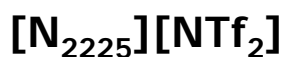
## Data and assumptions

- Bridge ions are only taken into account
  - Bridge concentration is ca 10x higher than the measured solutions
  - Arbitrary concentrations of  $\text{Et}_4\text{N}^+$  and  $\text{ClO}_4^-$  in measured solutions
- Mobilities and  $\Delta G$  of transfer
  - Pure solvents: literature data
    - Marcus, Kamlet, Taft, The Journal of Physical Chemistry, 1988, 92, 3613-3622
  - Mixed solvents: interpolations and COSMO-RS calculations
- Component (c): literature data and linear extrapolation (in mixed solvents)

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## Recent breakthrough: ILSB

- There is an ionic liquid (IL) for salt bridge (SB), which enables to (almost) cancel the parts **a** and **b**:



- A big part is testing the suitability of the IL for different solvents

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