Uued horisondid hapete-aluste uuringutes

Ivo Leito

ivo.leito@ut.ee

analytical.chem.ut.ee

Eesti Keemiaseltsi 100. aastapäev Tallinn 18.04.2019

pH

- Tuntuim parameeter happelisuse väljendamiseks:

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

- Igas lahustis (keskkonnas) on **solvateeritud prootoni aktiivsus** seotud tema **kontsentratsiooniga** just ***selles lahustis***

Standardolek

- **Standardolek** on 1 M (or 1 m) H^+ ***vastavas keskkonnas***

Standardolek on ***kontsentratsiooni-***põhine

- Sama H^+ kontsentratsioon **erinevates keskkondades** mõjutab protsesse **väga erinevalt**
  - Sest ***termodünaamiline happelisus*** (keemiline potentsiaal) on erinev

R. P. Buck et al *Pure Appl. Chem.* 2002, *74*, 2169

Keskkondade võime H^+ solvateerida on väga erinev

- Solvatasioon alandab H^+ **keemilist potentsiaali**
- H^+ ülekandevabaenergiad $\Delta G°_{tr}$ veest eri lahustitesse:

Lahusti	$\Delta G°_{tr}$ H_2O → lahusti (kJ/mol)
$MeNO_2$	95
MeCN	46
MeOH	10
Vesi	*0*
DMSO	-19
Püridiin	-28

- Üks pH ühik: 5.7 kJ/mol

Tulemus:

- Sama pH eri lahustites vastab väga erinevatele H^+ **keemilistele potentsiaalidele**:
  - Ja H^+ keemiline potentsiaal on see mis tüürib protsesse (katalüüs, redokspotentsiaal, happeline hüdrolüüs ...)

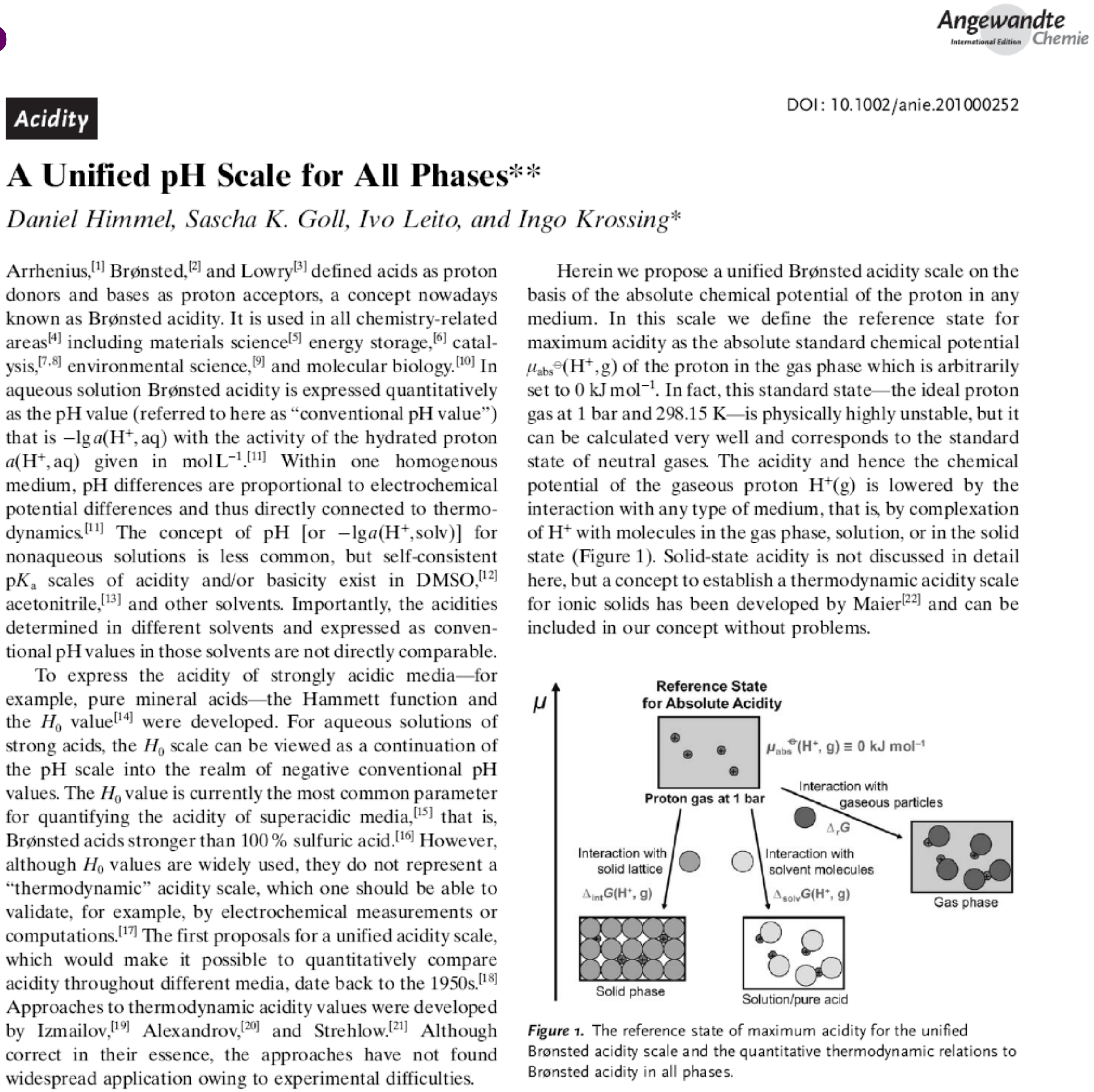
Näide:

pH 7	***püridiinis***	**aluseline**
pH 7	***vees***	**neutraalne**
pH 7	***atsetonitriilis***	**happeline**

A. Kütt et al *Tetrahedron Letters* 2018, *59*, 3738

Absoluutne pH?

- Standardolek: prootongaas 1 bar rõhul ($pH_{abs} = 0$)
- Defineeritud keemilise potentsiaali kaudu:



Angewandte Chemie International Edition

Acidity

DOI: 10.1002/anie.201000252

A Unified pH Scale for All Phases**

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

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

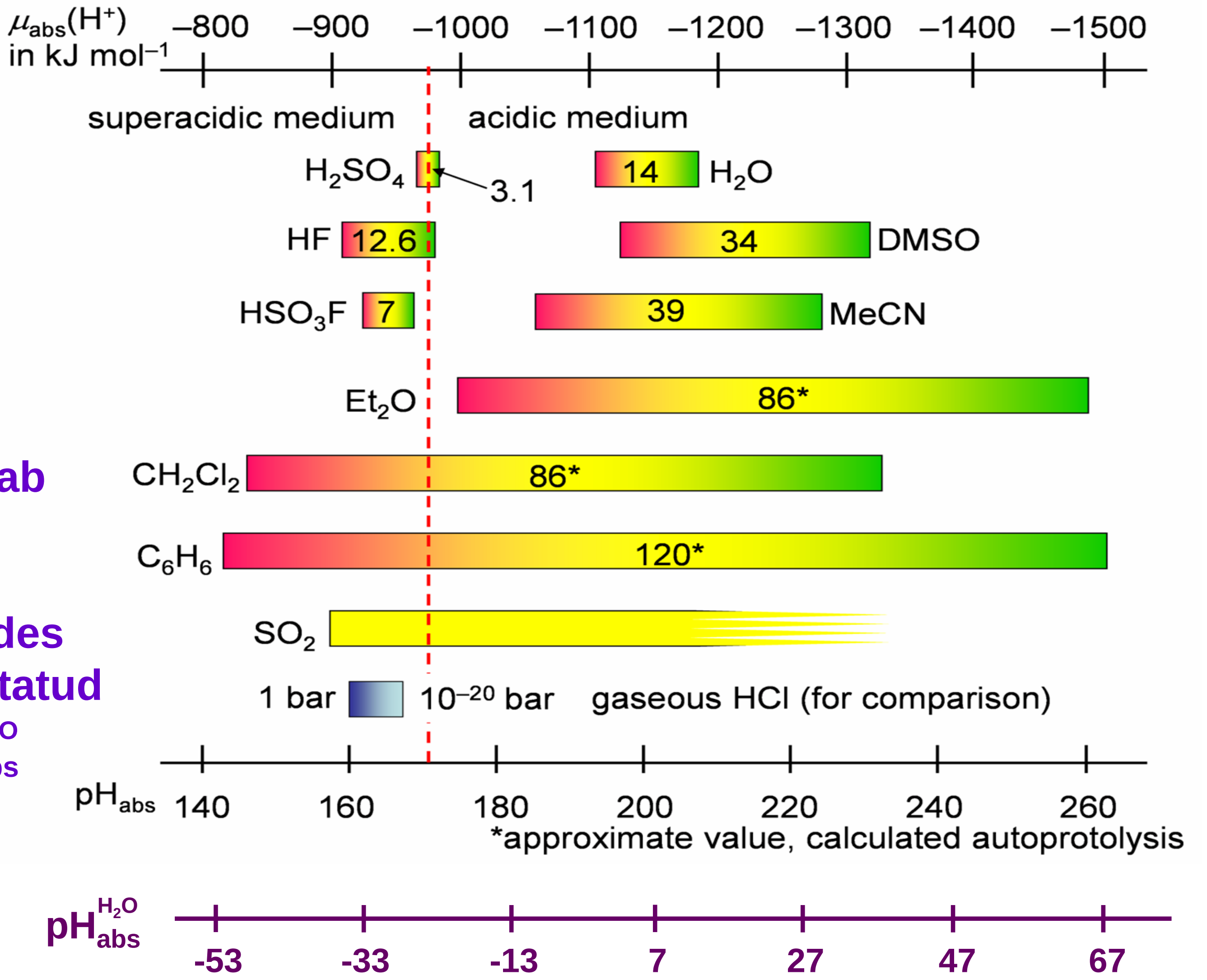
To express the acidity of strongly acidic media—for example, pure mineral acids—the Hammett function and the H_0 value[14] were developed. For aqueous solutions of strong acids, the H_0 scale can be viewed as a continuation of the pH scale into the realm of negative conventional pH values. The H_0 value is currently the most common parameter for quantifying the acidity of superacidic media,[15] that is, Brønsted acids stronger than 100% sulfuric acid.[16] 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.[17] 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.[18] Approaches to thermodynamic acidity values were developed by Izmailov,[19] Alexandrov,[20] and Strehlow.[21] 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 $\mu_{abs}^{\ominus}(H^+,g)$ of the proton in the gas phase which is arbitrarily set to $0\,kJ\,mol^{-1}$. 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 $H^+(g)$ is lowered by the interaction with any type of medium, that is, by complexation of 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[22] 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.

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

Happelisused eri keskkondades on võrreldavad



pH 7 vees vastab pH_{abs} 200.5

Mugavuse huvides Kasutatakse nihutatud skaalat: $pH_{abs}^{H_2O}$

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

Eelmise slaidi skeem oli (põhiosas) arvutuslik

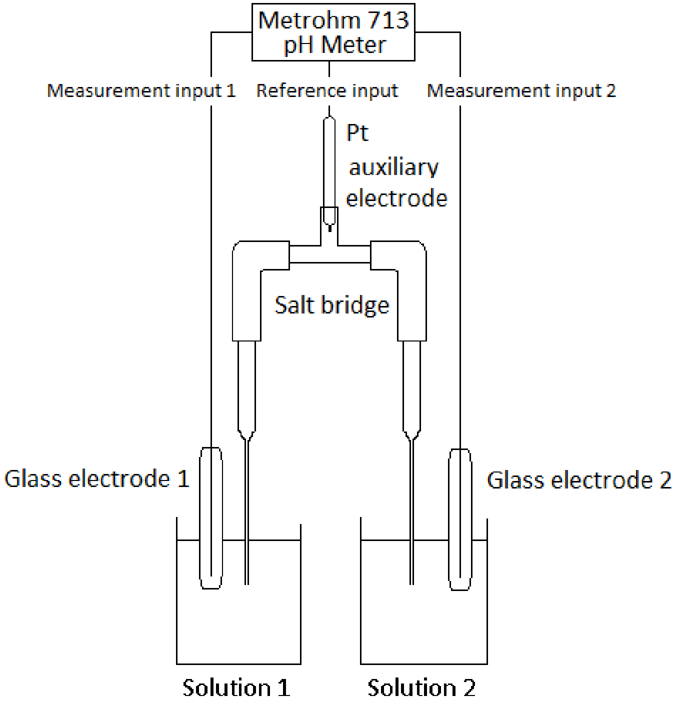
Kas pH_{abs} saab mõõta?

Kuidas pH_{abs} mõõta?

- Ilmne valik: **potentsiomeetria**
- Kuid on üsna tõsised probleemid:
  - **Mõõtmised on suhtelised**
    - Elektroodisüsteemi kõrge takistus
  - Erilahustite vahel mõõtes tekib väga kõrge **vedelik-vedelik piirpinna potentsiaal**
    - Keeruline elimineerida/arvesse võtta
  - **Madala polaarsusega lahustid on tülikad**
    - Madal juhtivus

Esimene eksperimentaalne realisatsioon

- **H_2O, MeOH, MeCN** ja segud
- **Diferentsiaalpotentsiomeetria** kasutades tahke kontaktiga klaaselektroode
- **LJP** hinnatud Izutsu mudeli baasil

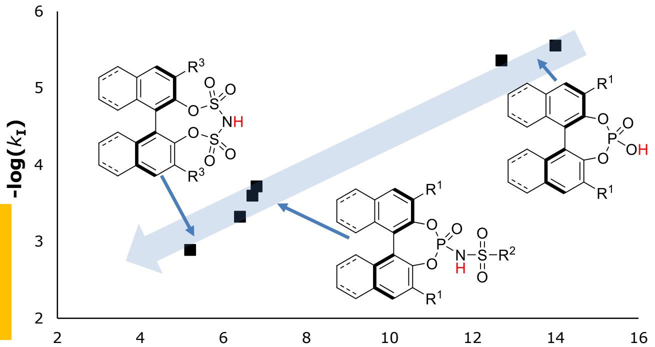


A. Suu et al *Anal. Chem.* 2015, *87*, 2623-2630

pH_{abs} rakendused?

Mittevedilahuste elektrokeemia

Happeline katalüüs

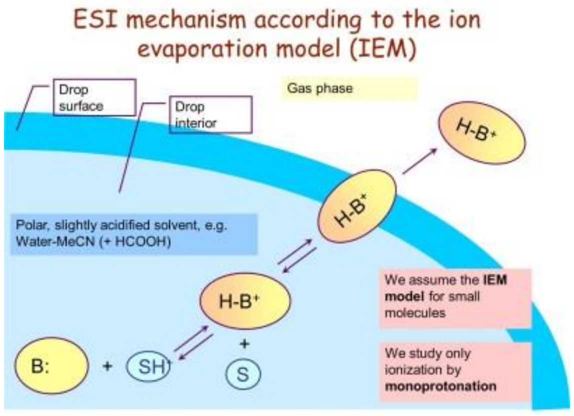


Happelisuse väljendamine keskkondades, kus solvateeritud H^+ sisaldus on ~olematu

Tahkete hapete happelisuse süsteemne väljendamine

pH_{abs}

Ionisatsiooniprotsessid MS ioonallikates


ESI mechanism according to the ion evaporation model (IEM)

Polar, slightly acidified solvent, e.g. Water-MeCN (+ HCOOH)

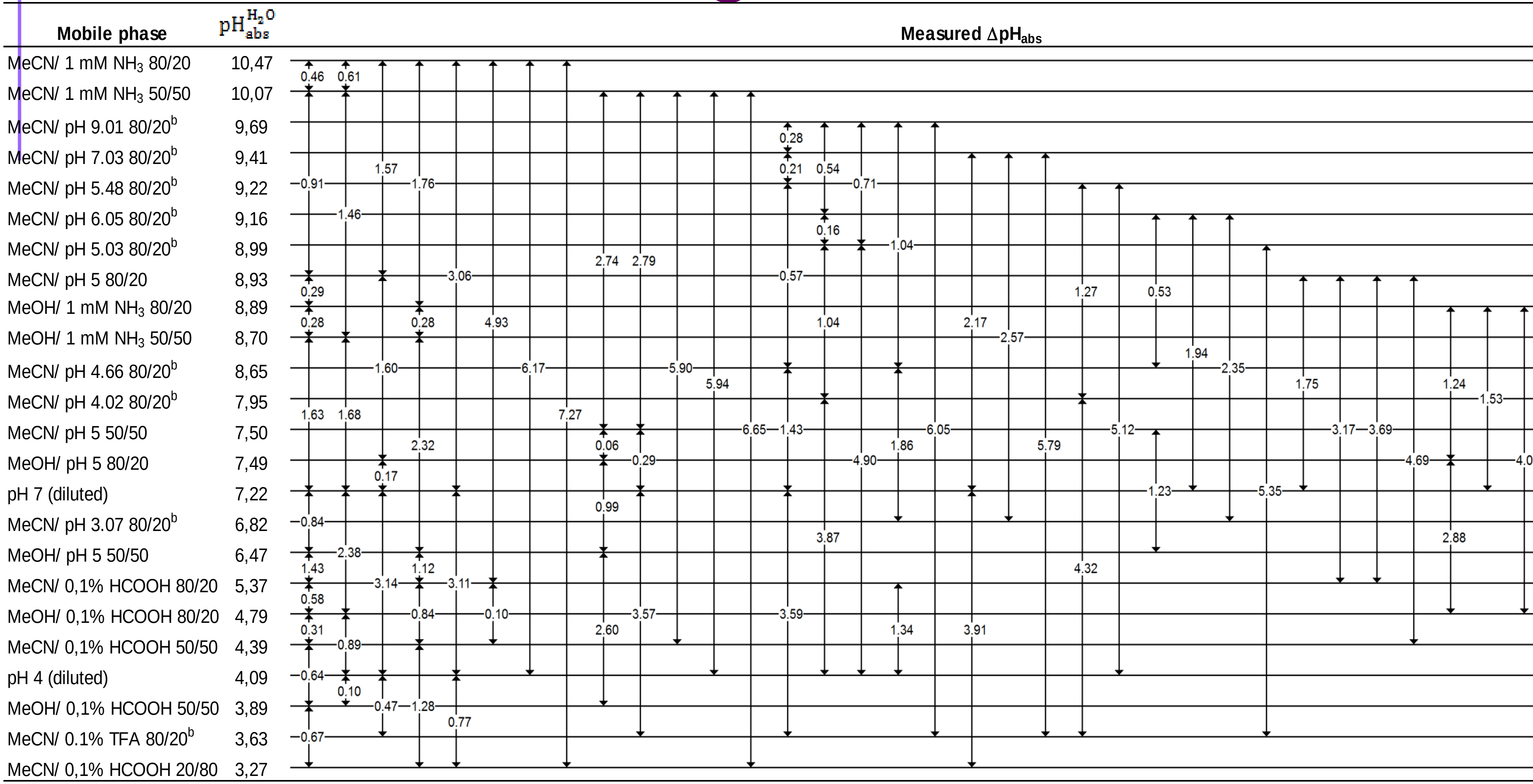
We assume the **IEM model** for small molecules

We study only ionization by **monoprotonation**

Happelisuse väljendamine mikroheterogeensetes süsteemides (biomembraanid, mitsellid, ...)

Vedelikkromatograafia mobiilfaaside happelisus

Vedelikkromatografia mobiilfaasid



Mobile phase	$pH_{abs}^{H_2O}$
MeCN/ 1 mM NH_3 80/20	10,47
MeCN/ 1 mM NH_3 50/50	10,07
MeCN/ pH 9.01 80/20^b	9,69
MeCN/ pH 7.03 80/20^b	9,41
MeCN/ pH 5.48 80/20^b	9,22
MeCN/ pH 6.05 80/20^b	9,16
MeCN/ pH 5.03 80/20^b	8,99
MeCN/ pH 5 80/20	8,93
MeOH/ 1 mM NH_3 80/20	8,89
MeOH/ 1 mM NH_3 50/50	8,70
MeCN/ pH 4.66 80/20^b	8,65
MeCN/ pH 4.02 80/20^b	7,95
MeCN/ pH 5 50/50	7,50
MeOH/ pH 5 80/20	7,49
pH 7 (diluted)	7,22
MeCN/ pH 3.07 80/20^b	6,82
MeOH/ pH 5 50/50	6,47
MeCN/ 0,1% HCOOH 80/20	5,37
MeOH/ 0,1% HCOOH 80/20	4,79
MeCN/ 0,1% HCOOH 50/50	4,39
pH 4 (diluted)	4,09
MeOH/ 0,1% HCOOH 50/50	3,89
MeCN/ 0.1% TFA 80/20^b	3,63
MeCN/ 0,1% HCOOH 20/80	3,27

- 83 suhtelist mõõtmist
- Skaala haare 7.25 pH ühikut, kooskõlalisus *s* = 0.14

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

Mobiilfaside happelisus

Mobiilfaas	$pH_{abs}^{H_2O}$	${}_{w}^{w}pH$
MeCN/ 1 mM NH_3 80/20	10.47	9.75
MeCN/ 1 mM NH_3 50/50	10.07	9.75
MeCN/ pH 5 80/20	8.93	5.00
MeOH/ 1 mM NH_3 80/20	8.89	9.75
MeOH/ 1 mM NH_3 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)[b]	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)[b]	4.09	4.15
MeOH/ 0.1% HCOOH 50/50	3.89	2.68

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

Happeline katalüüs apolaarsetes lahustites

- Mukaiyama aldol, Hosomi–Sakurai, Friedel–Crafts atsüülimine, Nazarovi tsüklseerimine, ...

Lahustid:
$C_2H_4Cl_2$, PhCl, CH_2Cl_2 ...

[redacted]

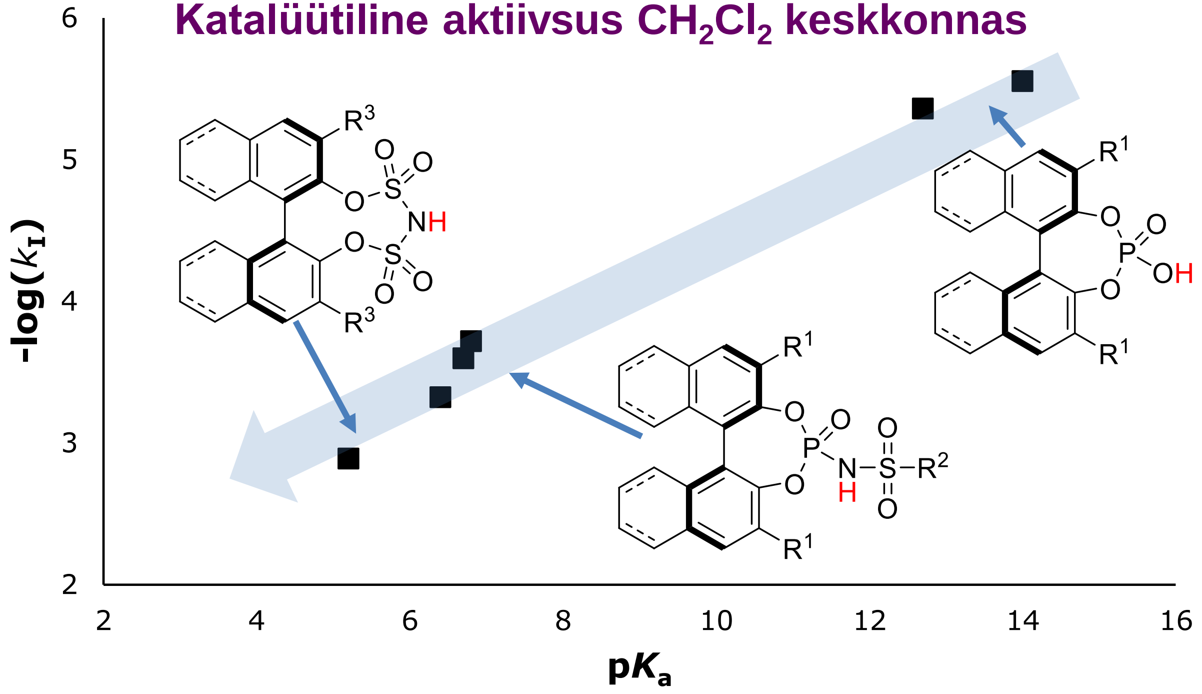
[redacted]

pK_a in DCE -15.4
pK_a in MeCN -2.8

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

H. Y. Bae et al *Nature Chem.* 2018, *10*, 888–894

Lahustid:
CH_2Cl_2

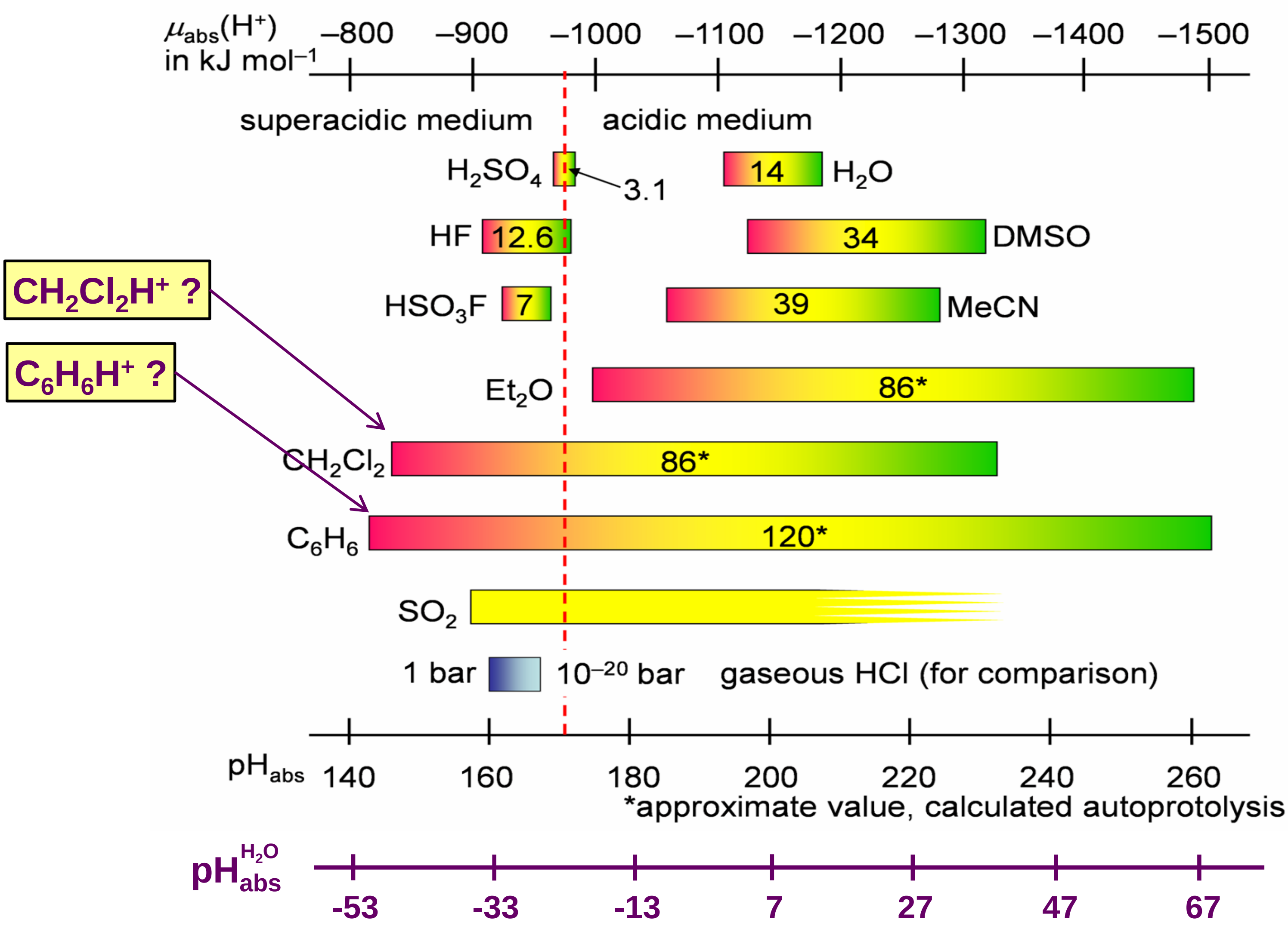


Katalüütiline aktiivsus CH_2Cl_2 keskkonnas

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

Mil määral mõjutab keskkonna happelisus?

Solvateeritud prootonid apolaarsetes keskkondades?



$CH_2Cl_2H^+$?

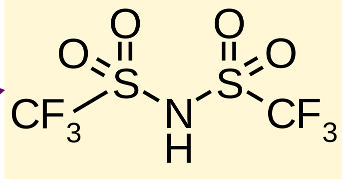
$C_6H_6H^+$?

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

pHabs 1,2-dikloroetaanis (1,2-DCE)

- $\varepsilon = 10$
- Kasutatav vähemalt $pH_{abs}^{H_2O} = -13$ -ni
- Seotud pH_{abs} skaalaga **Tf_2NH** kaudu
- **$DCEH^+$ praktiliselt puudub!**
    - Aga võivad olla protoneeritud lisandid

		$pK_{ip,r}$	$pK_{a,r}$	$pK_{a,DCE}$	$pH_{abs}^{H_2O}$
66	TfOH	-11.4	-11.3	33.7	-9.0
67	$C_6H_5SO(=NTf)NHTf$	-11.5	-11.7	33.3	-9.4
68	$TfCH(CN)_2$	-11.6	-11.5	33.5	-9.2
69	Br-TCNP	-11.8	-11.8	33.2	-9.5
70	$[C(CN)_2=C(CN)]_2NH$	-11.8	-12.0	33.0	-9.7
71	$3,5\text{-}(CF_3)_5\text{-}C_6H_3\text{-TCNP}$	-11.8	-12.0	33.0	-9.7
72	Tf_2NH [f]	-11.9	-12.0	33.0	-9.7
73	$4\text{-Cl-}C_6H_4SO(=NTf)NHTf$	-12.1	-12.3	32.7	-10.0
74	Cl-TCNP	-12.1	-12.1	32.9	-9.8
75	$(C_3F_7SO_2)_2NH$	-12.1	-12.3	32.7	-10.0
76	$(C_4F_9SO_2)_2NH$	-12.2	-12.4	32.6	-10.1
77	$CN\text{-}CH_2\text{-TCNP}$	-12.3	-12.4	32.6	-10.1
78	$(C_2F_5SO_2)_2NH$	-12.3	-12.4	32.6	-10.1
79	$CF_3\text{-TCNP}$	-12.7	-12.8	32.2	-10.5
80	$HClO_4$	-13.0	-12.8	32.2	-10.5
81	$CF_2(CF_2SO_2)_2NH$	-13.1	-13.1	31.9	-10.8
82	$4\text{-NO}_2\text{-}C_6H_4SO(=NTf)NHTf$	-13.1	-13.3	31.7	-11.0
83	$HB(CN)_4$	-13.3	-13.3	31.7	-11.0
84	$(FSO_2)_3CH$	-13.6	-13.6	31.4	-11.3
85	$Tf_2CH(CN)$	-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

Suur Tänu kõigile!

Peategelased:

Agnes Heering, Valentin Radtke, Andreas Ermantraut, Jaak Nerut, Rasmus Born, Daniel Himmel, Ingo Krossing

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

ja kõik UnipHied partnerid!

UnipHied

EMPIR EURAMET

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

European Union
Regional Development Fund

Investing in your future

Rahastus:
EU Regional Development Fund
(TK141 “Advanced materials and high-technology devices for energy recuperation systems”),
UT Institutional funding project IUT20-14, by the European Research Council (ERC) with the Advanced Grant “UniChem”, No. 291383.

analytical.chem.ut.ee