Comparison of Redox Potentials in Non-Aqueous Solvents: Silver is not a Noble Metal in the Acidic Ionic Liquid HmimBr

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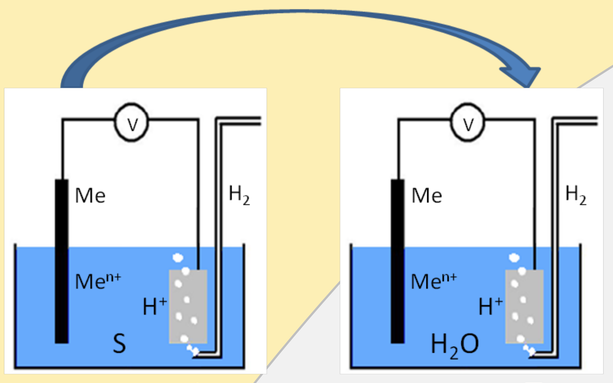
The determination of comparable redox potentials over solvent barriers is a long discussed topic.[1,2] We recently introduced the Protoelectric Potential Map (PPM) which presents a new combined pH- and redox scale in an absolute sense.[3,4] The PPM is thermodynamically well described and allows one to compare and predict stabilities and reaction behavior of any species in any media. One impressive example of the influence of the media and pH value is the behavior of silver in acidic HmimBr. Our calculations show that Ag^+/Ag has a lower E° than H^+/H_2 indicating its non-noble character under these conditions. We could proof this experimentally by the redox potential of Ag^+/Ag vs. RHE and observed the dissolution of a piece of silver in acidic HmimBr. Our intention is to establish the SHE in HmimBr. Combined with the energy of transfer of the proton from water to HmimBr we are able to introduce absolute redox potential values.

Key to correlate redox scales

Gibbs energy of transfer[5] of any species for each medium

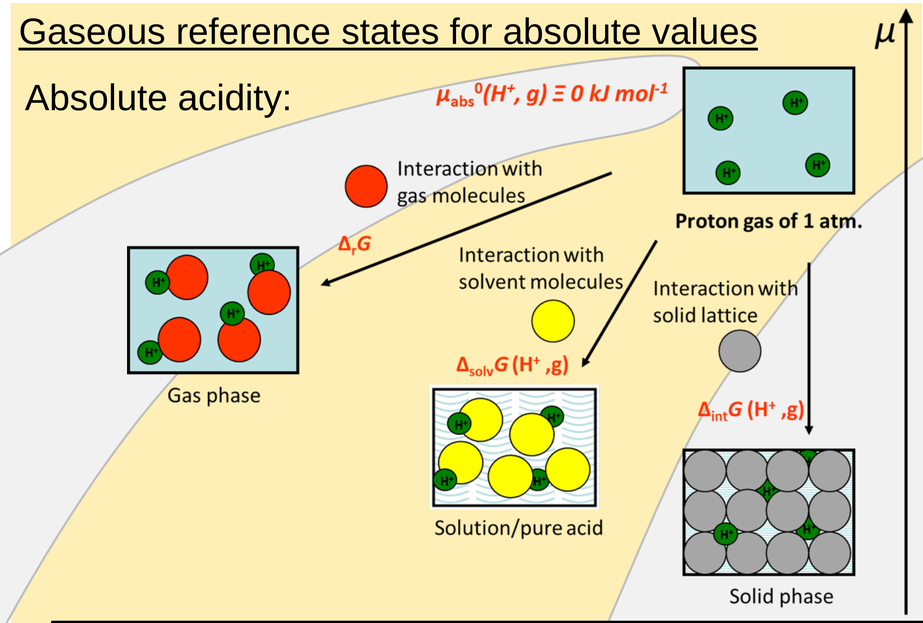


$$\Delta G = -zF\Delta E \qquad \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_{j\neq i}}$$

$$\mu_{abs}^{\circ}(H^+, solv) = \Delta_{solv}G^{\circ}(H^+, g \rightarrow med)$$

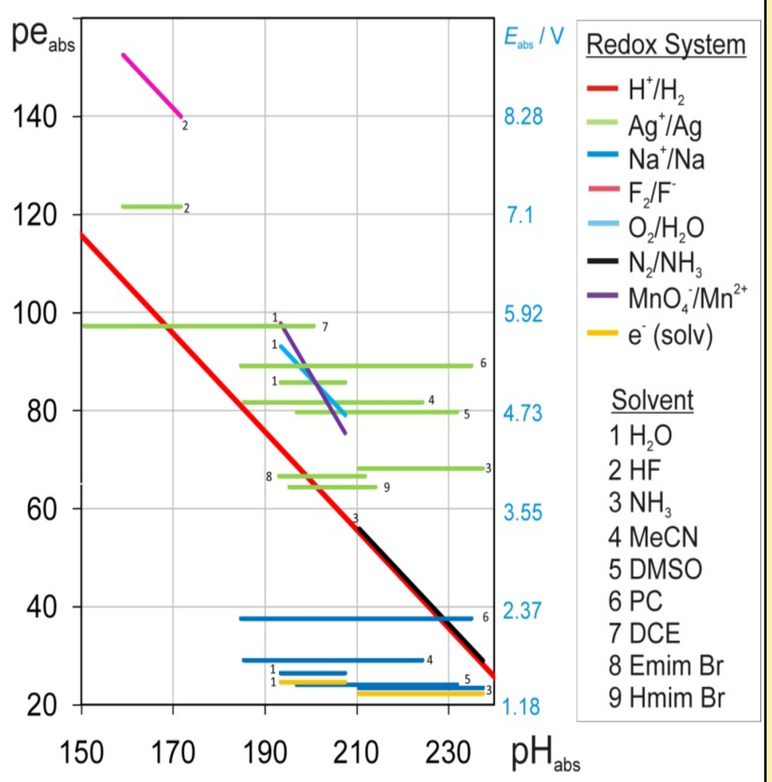
Gaseous reference states for absolute values

Absolute acidity:



Protoelectric Potential Map (PPM)

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



pe_abs

Decreasing Reducity

Standard conditions: Reference state for absolute redox potentials

Decreasing Acidity

pH_abs

Standard conditions: Reference state for absolute Brønsted acidity

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

Analogously to the acidity we define the reduction potential

Definition acidity: $pH = -\lg a(H^+, solv)$

Definition reducity: $pe = -\lg a(e^-, solv)$

The difference of one pH or pe unit is changing μ(H^+) or μ(e^-) about a fixed amount:

$$\Delta pH = \Delta pe = 1 \equiv RT\ln 10 = 5{,}71\frac{kJ}{mol} \quad (T = 298{,}15\ K)$$

Anchor point

Gibbs solvation energy of the proton in H_2O [6,7]

$$\Delta_{H_2O}G^{\circ}(H^+) = -1104{,}5 \pm 8\frac{kJ}{mol}$$

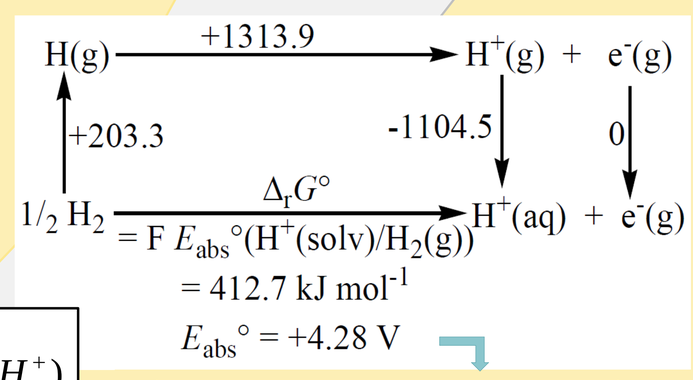
pH_{abs}=193,4 (pH=0)

Absolute Acidity[4]

$$\Delta_{solv}G^{\circ}(H^+, S) = -1104{,}5\frac{kJ}{mol} + \Delta_{tr}G^{\circ}(H^+, H_2O \rightarrow S)$$

Absolute potential of the SHE

Standard hydrogen electrode (SHE) in H_2O by the Born-Haber-Fajans-Cycle (BHFC)



pe_{abs}= 72,2 (1 bar H_2, pH=0)

Silver in HmimBr - Correlation to SHE

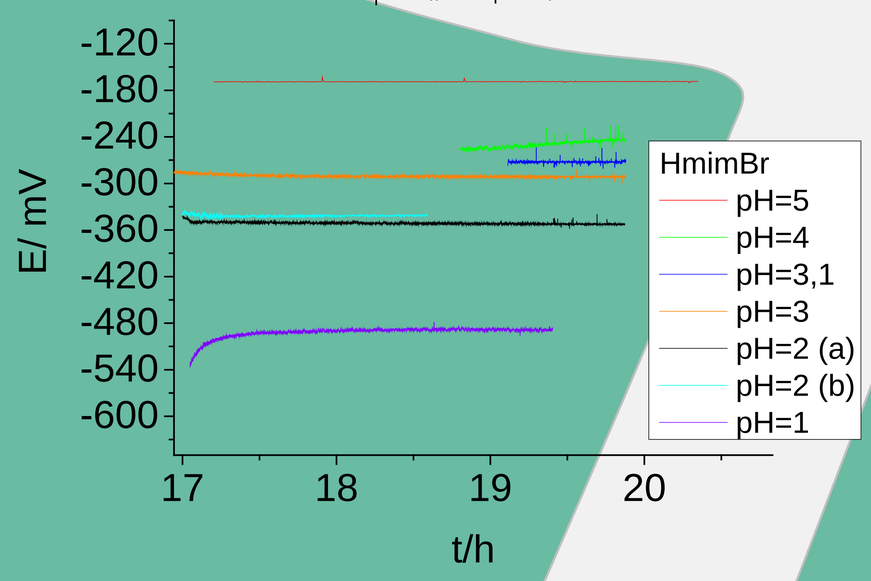
Calculated values via COSMO-RS:

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

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

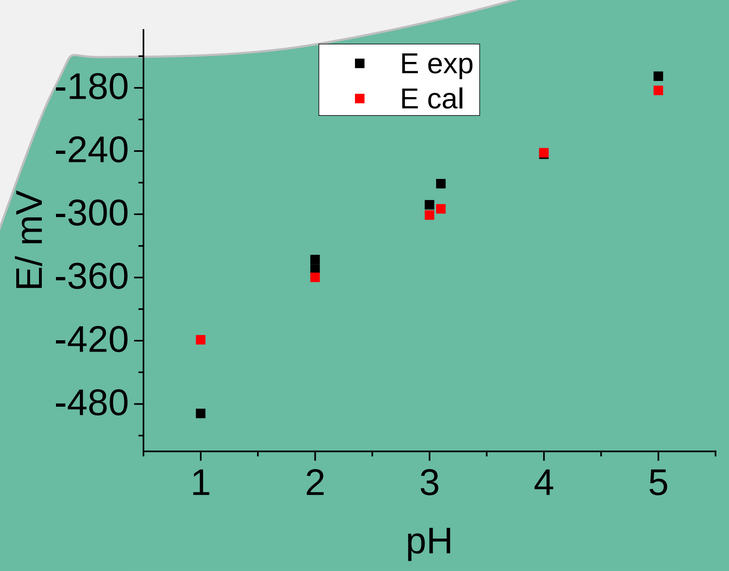
$$\Delta E_{abs}^{\circ}(Ag^+/Ag \quad vs. \quad H^+/H_2) = -360\ mV$$

$$Ag^+|Ag\,\|H^+|H_2|Pt$$



Ag[Al(OC(CF_3)$_3$)$_4$] 0,01 M
Variation of pH via HBr concentration

Nernstian behavior of the RHE in HmimBr

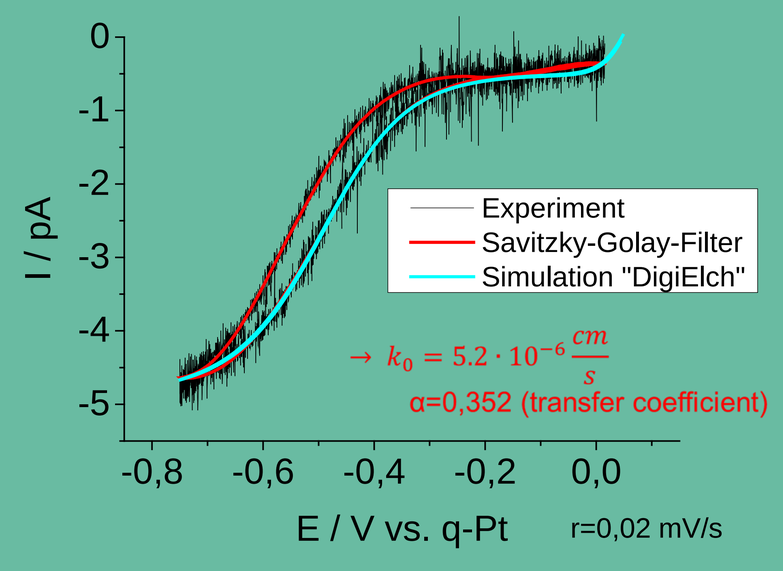


Calculation

$$\Delta E = \Delta E_{abs}^{\circ} + \frac{RT}{zF}\ln a(Ag^+) + 59{,}16mV \cdot pH$$

$$\Delta E = -478{,}25mV + 59{,}16mV \cdot pH$$

Kinetic of HBr_2^- electronation at Pt (a_{eff}=9.18 µm)



$\rightarrow k_0 = 5.2 \cdot 10^{-6}\frac{cm}{s}$

α=0,352 (transfer coefficient)

$$I_{SS} = 4zFDca_{eff} = -4{,}77\ pA \quad \rightarrow D = 1{,}21\cdot 10^{-7}\frac{cm^2}{s}$$

$$c(HBr_2^-) = 0{,}01\ M$$

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