

Supporting Information

Hydrogen and Hydrogen Peroxide Formation in Trifluorotoluene- Water Biphasic System

Wojciech Adamiak,^{a*} Justyna Jedraszko,^a Olga Krysiak,^a Wojciech Nogala,^a Jonnathan C.

Hidalgo-Acosta,^b Hubert H. Girault,^b Marcin Opallo^{a*}

^a Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

^b Laboratoire d'Electrochimie Physique et Analytique, Ecole Polytechnique Federale de Lausanne, CH-
1015 Lausanne, Switzerland

Calculation of the Galvani potential difference between TFT and W

Assuming that (1) volumes of TFT and W phase are equal, and (2) ion activities are equal to their concentrations, the Galvani potential difference between TFT and W can be calculated from the equation:¹

$$\sum_{i=1} \frac{z_i c_i^0(W)}{1 + \exp\left[\left(\frac{z_i F}{RT}\right)(\Delta_W^{\text{TFT}} \phi_i^\ominus - \Delta_W^{\text{TFT}} \phi)\right]} + \sum_{i=1} \frac{z_i c_i^0(\text{TFT})}{1 + \exp\left[\left(\frac{z_i F}{RT}\right)(\Delta_W^{\text{TFT}} \phi_i^\ominus - \Delta_W^{\text{TFT}} \phi)\right]} = 0 \quad (\text{s1})$$

where $c_i^0(W)$, $c_i^0(\text{TFT})$ are initial concentrations of ion i in W and TFT phase, respectively. Table S1 lists transfer potentials and initial concentrations of ions present in the studied TFT-W biphasic system necessary to solve eq. (s1). The calculated $\Delta_W^{\text{TFT}} \phi$ is equal -0.447 V.

Table S1. Standard transfer potentials ($\Delta_W^{\text{TFT}} \phi_i^\ominus$) and concentrations of ions in the TFT-W biphasic system with BATB in TFT.

Ion, i	$\Delta_W^{\text{TFT}} \phi_i^\ominus / \text{V}$	$c_i^0(W) / \text{M}$	$c_i^0(\text{TFT}) / \text{M}$
BA ⁺	0.636 ^a	0	0.005
H ⁺	-0.523	0.1	0
TB ⁻	-0.616	0.005	0.005
Li ⁺	-0.650 ^a	0.005	0
ClO ₄ ⁻	0.235	0.1	0

^a Calculated from eq. (4) and (6) in the paper with $\Delta_W^{\text{DCE}} G_{\text{BA}^+}^\ominus = -64.6 \text{ kJ mol}^{-1}$ and $\Delta_W^{\text{DCE}} G_{\text{Li}^+}^\ominus = 62.7 \text{ kJ mol}^{-1}$ ⁵

Calculation of HTB and H⁺ concentrations in TFT

Transfer of HTB from W to TFT is described by the reaction:



whose $\Delta G^\ominus = -40.7 \text{ kJ mol}^{-1}$. The equilibrium constant

$$K_1 = \frac{[\text{HTB}]_{(TFT)}}{[\text{H}^+]_{(W)}[\text{TB}^-]_{(W)}} \quad (\text{s3})$$

where $[\text{HTB}]_{(TFT)}$ is the equilibrium concentration of HTB in TFT, $[\text{H}^+]_{(W)}$ and $[\text{TB}^-]_{(W)}$ are equilibrium concentrations of H⁺ and TB⁻ in W, respectively, can be calculated as

$$K_1 = \exp\left(-\frac{\Delta G^\ominus}{RT}\right) = 1,35 \times 10^7 \quad (\text{s4})$$

Since the volumes of both liquid phases are equal, one can substitute:

$$[\text{H}^+]_{(W)} = c_{\text{H}^+}^0_{(W)} - [\text{H}^+\text{TB}^-]_{(TFT)} \quad (\text{s5})$$

$$[\text{TB}^-]_{(W)} = c_{\text{TB}^-}^0_{(W)} - [\text{H}^+\text{TB}^-]_{(TFT)} \quad (\text{s6})$$

to equation (s3). Next, by taking $K_1 = 1,35 \times 10^7$, $c_{\text{H}^+}^0_{(W)} = 0.1 \text{ mol dm}^{-3}$, $c_{\text{TB}^-}^0_{(W)} = 0.005 \text{ mol dm}^{-3}$ one solves eq. (s3) to obtain $[\text{H}^+\text{TB}^-]_{(TFT)} = 0.005 \text{ mol dm}^{-3}$. This means that TB⁻ transfer H⁺ stoichiometrically from W to TFT.

The concentration of H⁺ and TB⁻ in TFT can then be calculated from HTB dissociation equilibrium:



The equilibrium constant

$$K_2 = \frac{[\text{H}^+]_{(TFT)}[\text{TB}^-]_{(TFT)}}{[\text{HTB}]_{(TFT)}} \quad (\text{s8})$$

can be calculated as:

$$K_2 = \exp\left(\frac{\Delta_{\text{as}}G}{RT}\right) = 2.68 \times 10^{-6} \quad (\text{s9})$$

where $\Delta_{\text{as}}G$ is the association energy calculated from equation (15) in the paper and equal to $-31.8 \text{ kJ mol}^{-1}$. By substituting

$$[\text{HTB}]_{(\text{TFT})} = c_{\text{HTB}(\text{TFT})}^0 - [\text{H}^+]_{(\text{TFT})} \quad (\text{s10})$$

$$[\text{H}^+]_{(\text{TFT})} = [\text{TB}^-]_{(\text{TFT})} \quad (\text{s11})$$

to eq. (s8) and taking $K_2 = 2.68 \times 10^{-6}$, $c_{\text{HTB}(\text{TFT})}^0 = 0.005 \text{ mol dm}^{-3}$, one calculates $[\text{H}^+]_{(\text{TFT})} = [\text{TB}^-]_{(\text{TFT})} = 0.0001 \text{ mol dm}^{-3}$. This corresponds to the degree of HTB dissociation of 2%.

References

[s1] Volkov, A. E. G. *Liquid Interfaces in Chemical, Biological and Pharmaceutical Applications*; Marcel Dekker: New York, 2001.