

Exercise: calculate the overpotential in the Fe-porphyrin system

Recall experimental conditions:

In DMF; $[\text{Et}_3\text{NH}]\text{Cl}$ as acid; Working potential at -1.6 V vs. SCE

As $\text{Fc}/\text{Fc}^+ = 0.47$ vs. SCE in DMF

$E(\text{working}) = -1.6$ vs. SCE = -2.07 V vs. Fc/Fc^+

How about the thermodynamic potential of HER using $[\text{Et}_3\text{NH}]\text{Cl}$ in DMF?

Answer:

$\text{p}K_a([\text{Et}_3\text{NH}]^+)$ in DMF = 9.2

$E^\circ_{\text{H}^+} = -0.77$ vs. Fc/Fc^+

$E([\text{Et}_3\text{NH}]^+) = -1.31$ vs. Fc/Fc^+

The overpotential of the Fe-porphyrin system is therefore 0.76 V

This is a rather big overpotential;

it was dictated by the potential to reduce $\text{Fe}(\text{I})$ to $\text{Fe}(\text{0})$.