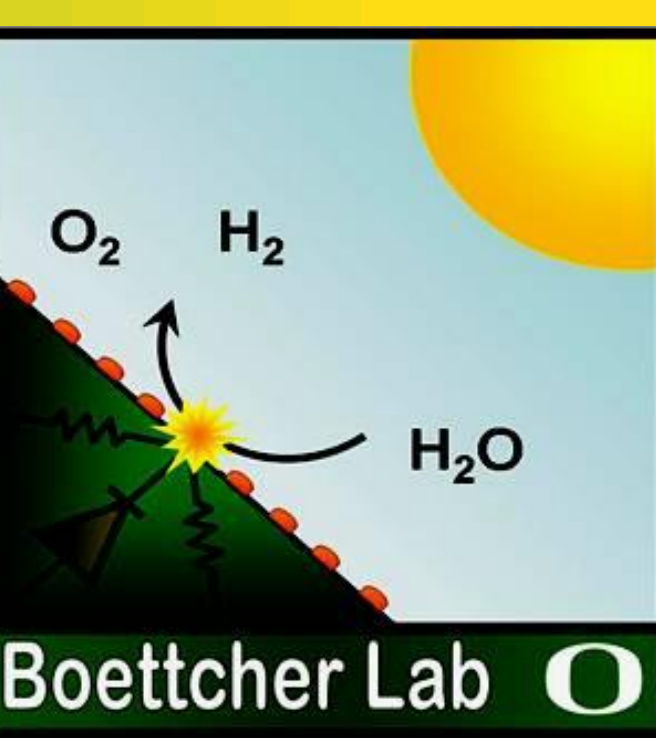




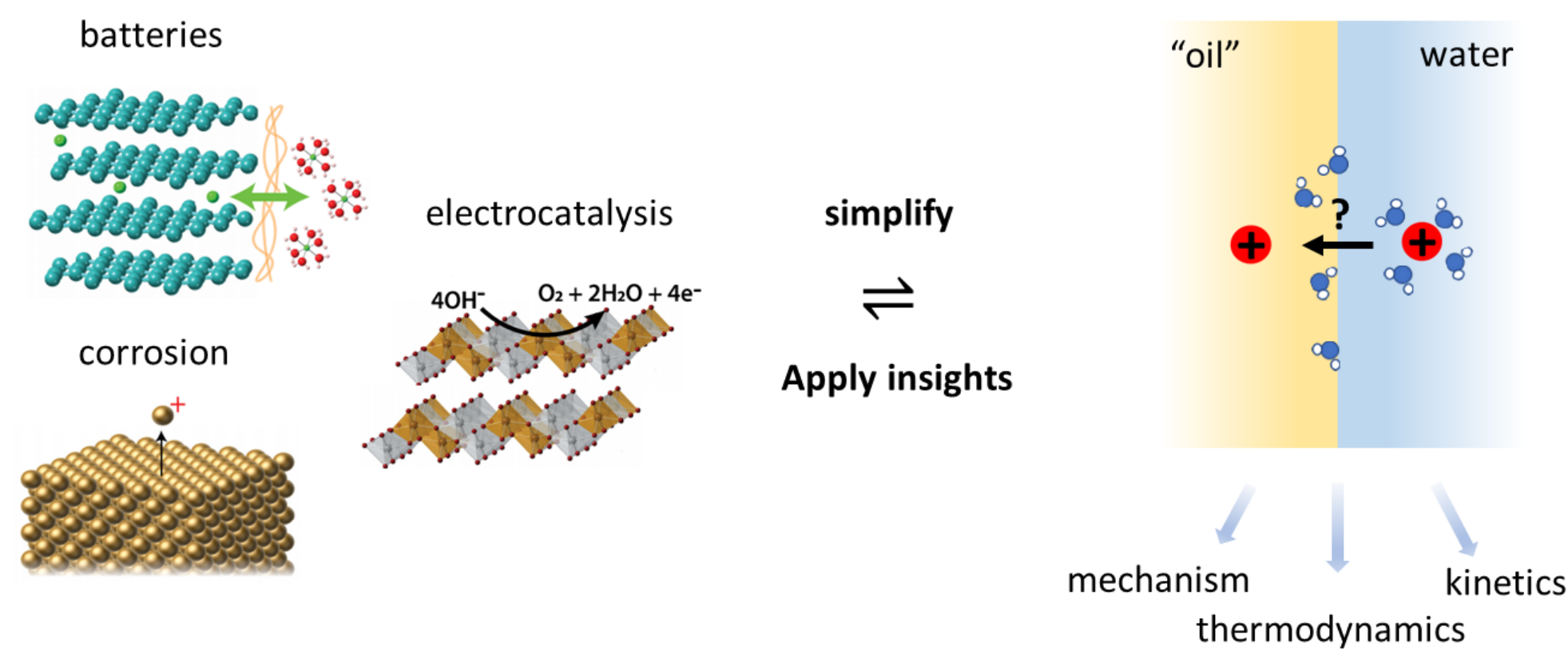
# Kinetic Isotope Effect Suggests Mechanistic Differences in Facilitated Proton Transfer at the Interface Between Two Immiscible Electrolyte Solutions (ITIES)

Nick D'Antona<sup>1</sup>, Paul Kempler<sup>1,2</sup>, Shannon Boettcher<sup>1,2</sup>

<sup>1</sup>Department of Chemistry, University of Oregon <sup>2</sup>Oregon Center for Electrochemistry



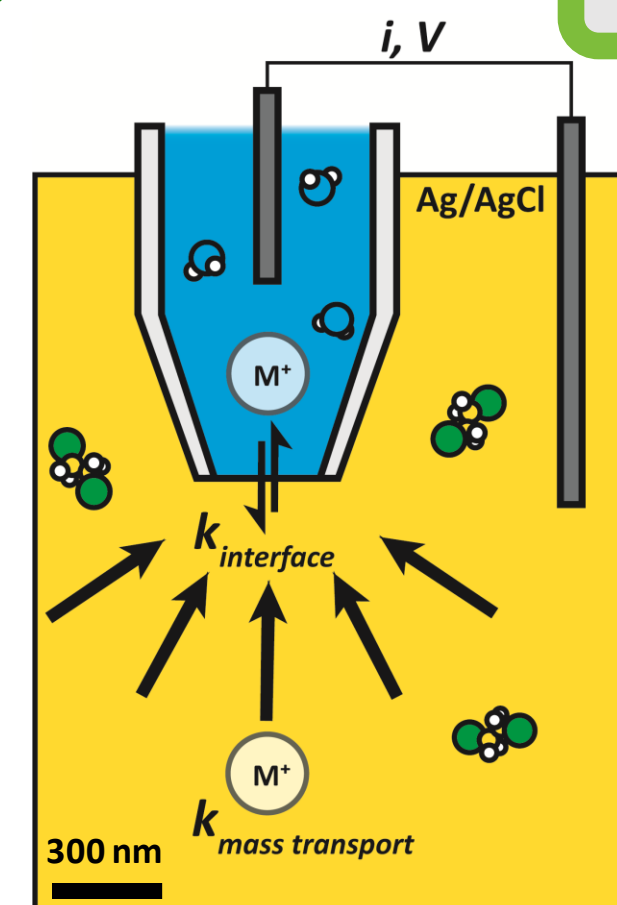
## Interfacial ion transfer



### Interfacial Ion Transfer is everywhere

- From batteries to electrocatalysts to corrosion, ionic processes tend to be rate limiting
- The ITIES is useful for studying ionic processes independent of electrode surface chemistry

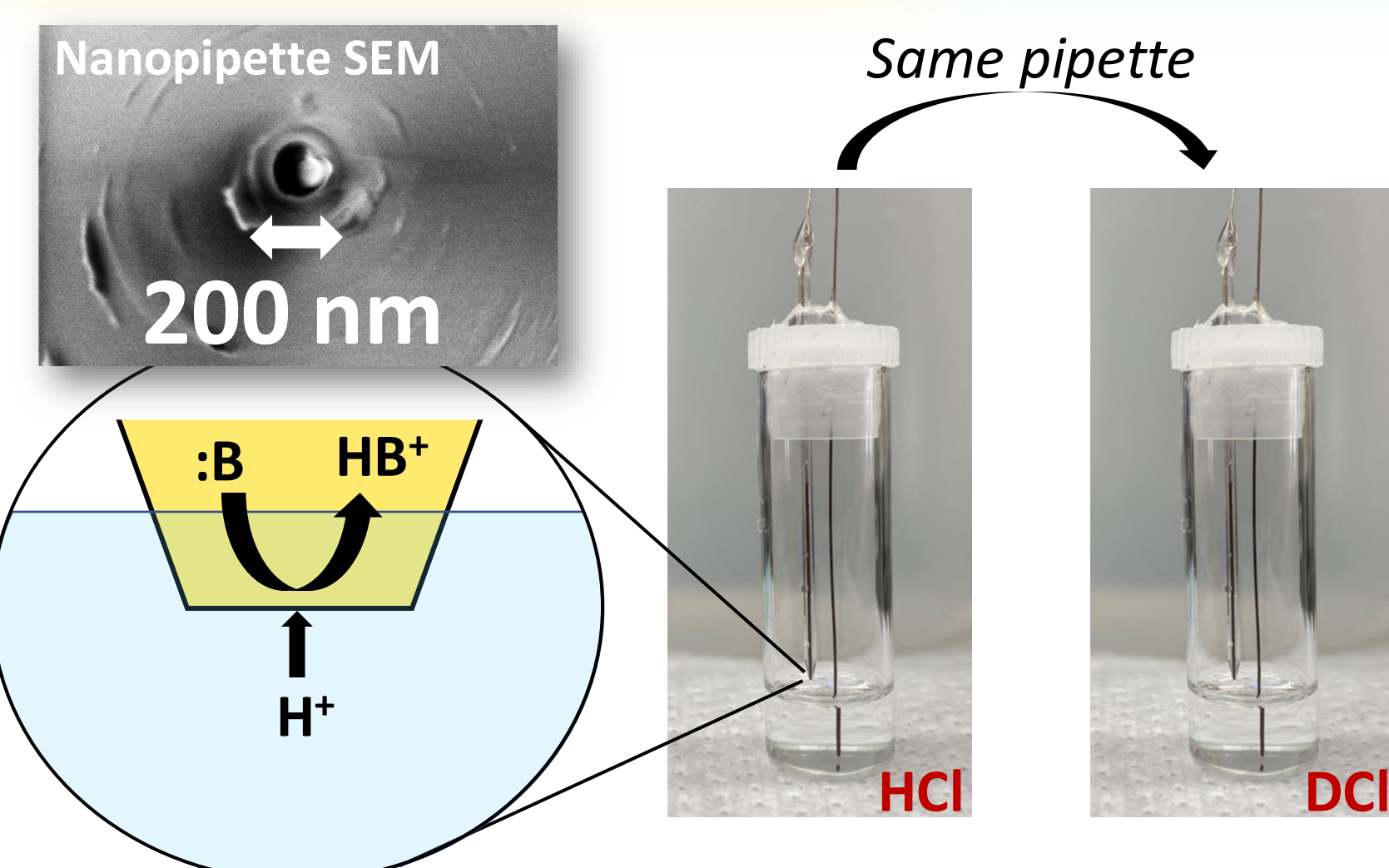
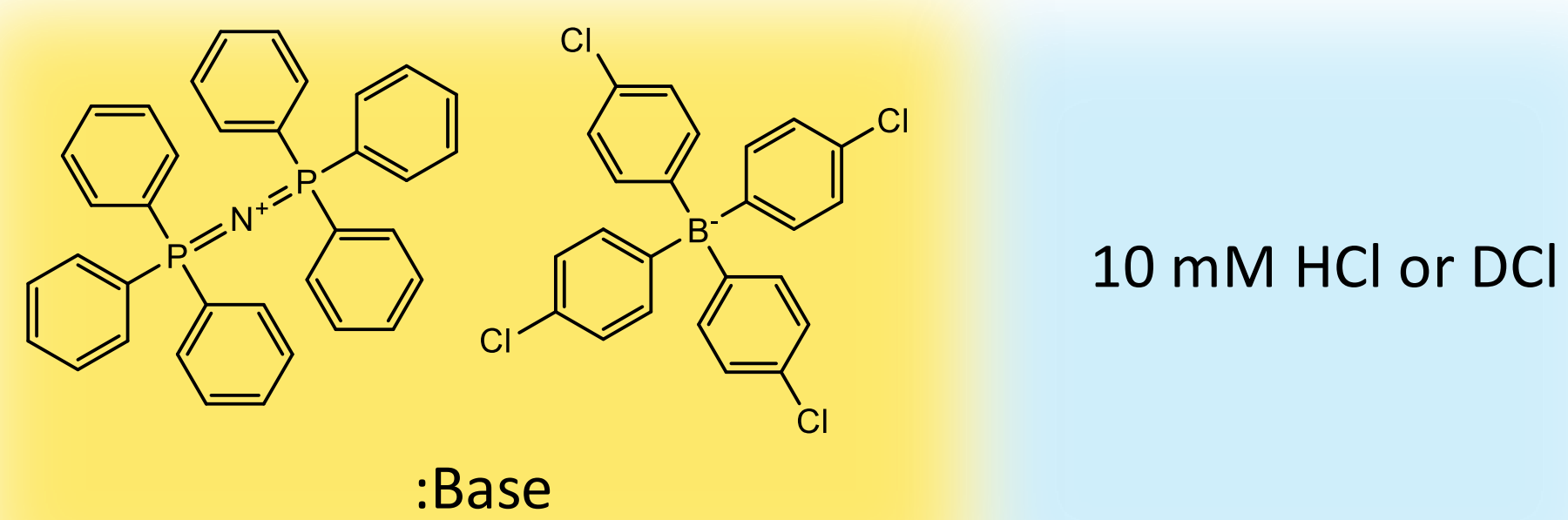
## Nanopipette experiment



### Ion transfer mechanisms at the ITIES are hard to study

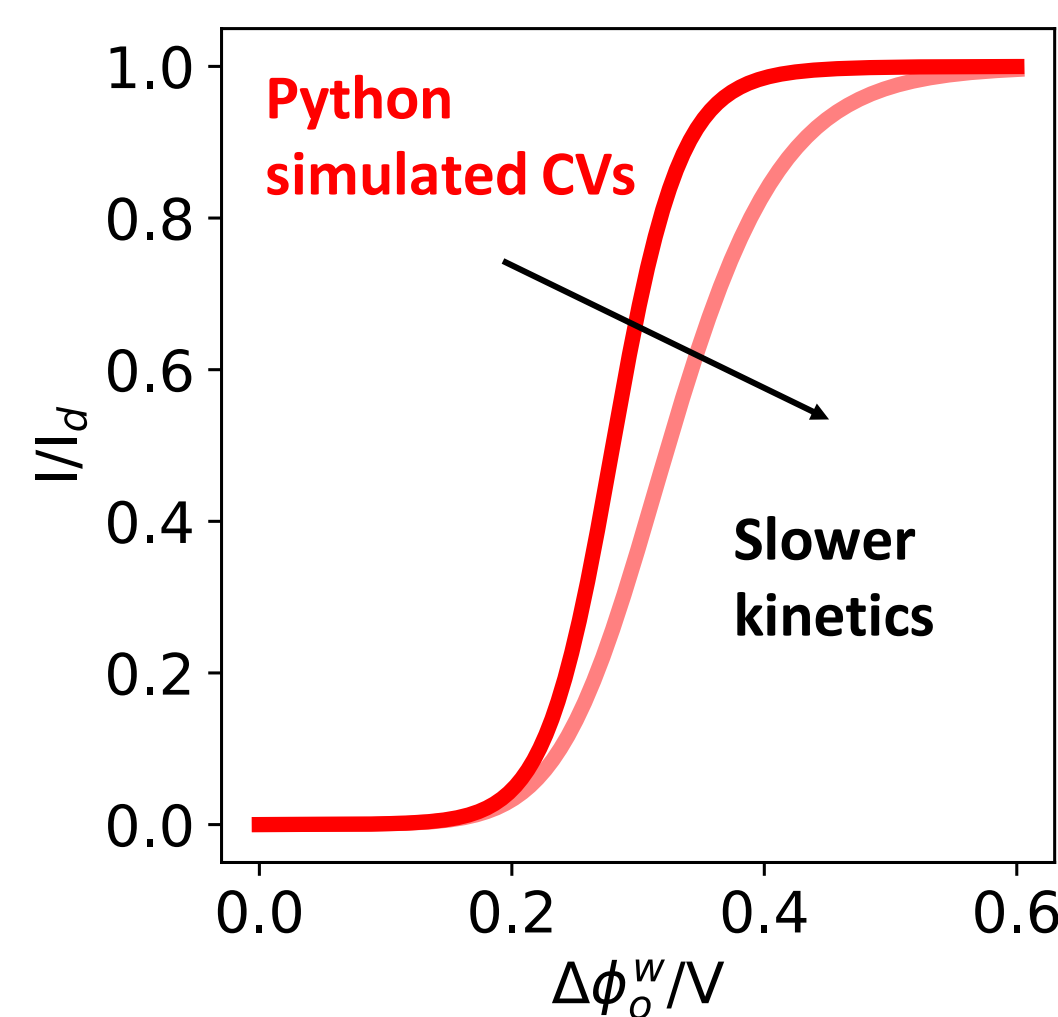
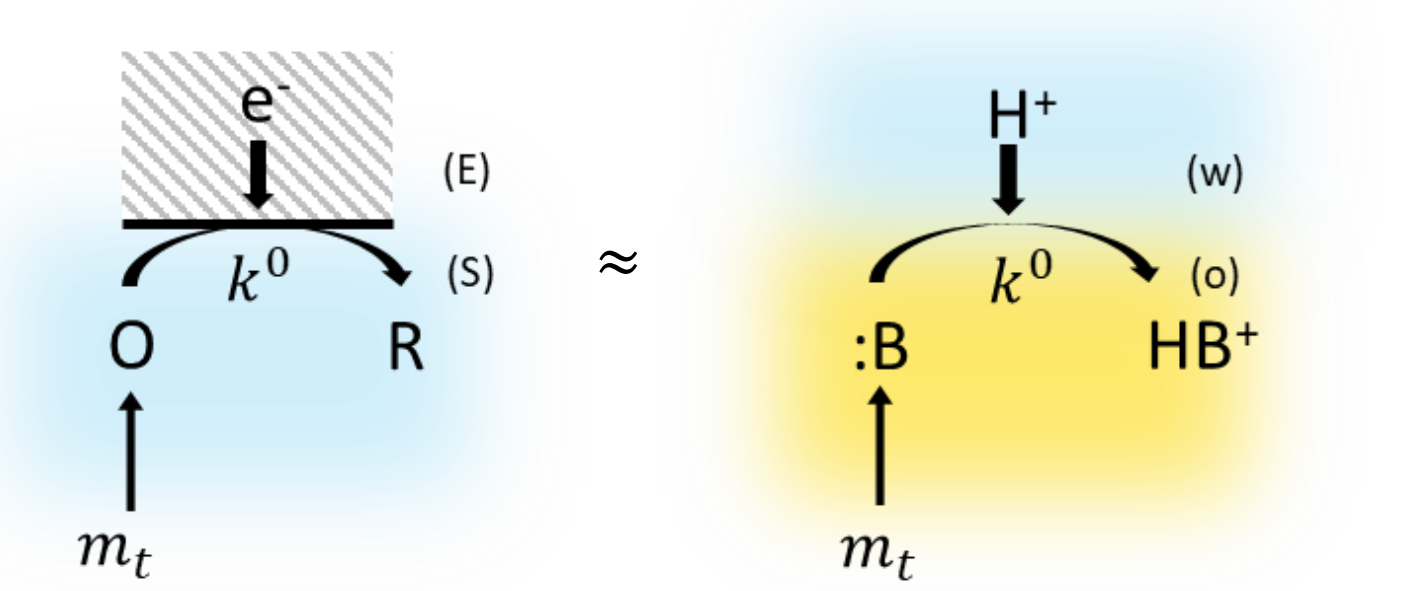
- Ultrafast interfacial kinetics necessitate the use of nanopipette electrodes to enhance mass transport

## Organic electrolyte + hydrophobic base (ionophore) | Aqueous electrolyte



## Steady state voltammetry reveals kinetic limitations

Electron transfer (solid liquid interface) | Facilitated proton transfer (liquid-liquid interface)



$$\frac{i}{i_d} = \frac{1}{1 + \theta}$$

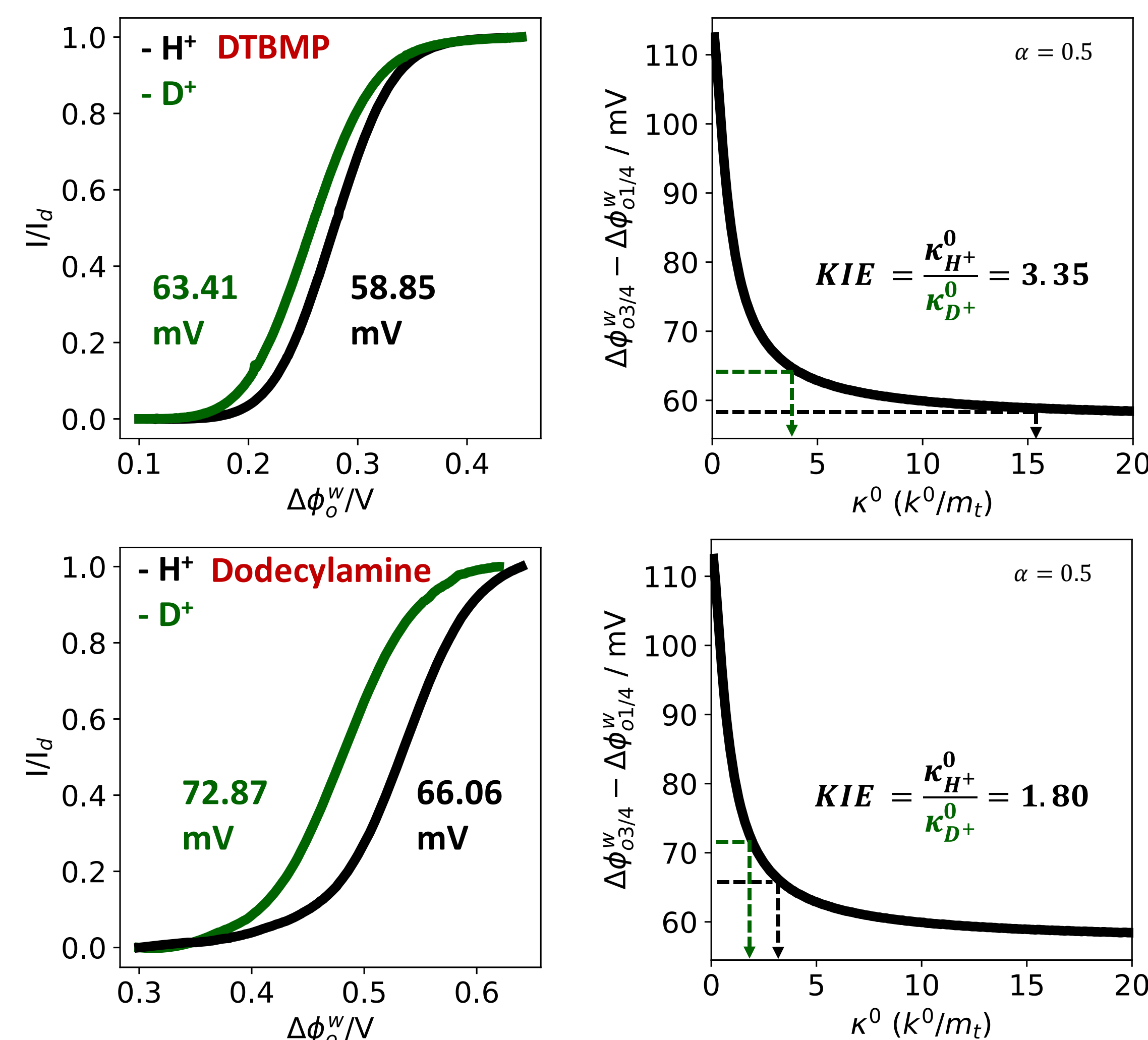
$$\theta = 1 + e^{\frac{F}{RT}(\Delta\phi_o^{w0'} - \Delta\phi_o^{w0})}$$

$$\kappa = \frac{k^0}{m_t} e^{\frac{\alpha F}{RT}(\Delta\phi_o^{w0} - \Delta\phi_o^{w0'})}$$

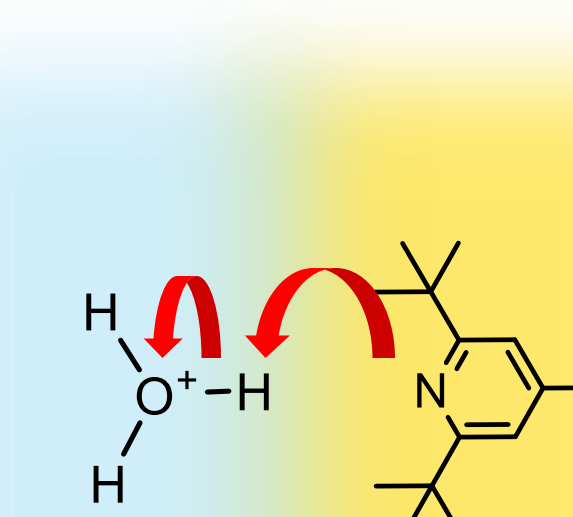
### Electrochemical model

- Equation describes steady state quasireversible electron transfer where "R" is initially absent
- This model is analogous to facilitated proton transfer at the liquid-liquid interface provided that  $[H^+]_{aq}$  is high and only :B is initially present
- When the ratio of the standard rate constant to the mass transfer coefficient ( $k^0/m_t$ ) is low, usually less than 10, the voltametric wave appears more "tilted" because the kinetics are no longer reversible with respect to mass transport-- ie.  $\Delta\phi_o^{w0'} - \Delta\phi_o^{w0} > 56.4 \text{ mV}$
- For a given value of the charge transfer coefficient  $\alpha$ , the measured  $\Delta\phi_o^{w0'} - \Delta\phi_o^{w0}$  is associated with a single value of  $k^0/m_t$  (see figure 1b below)

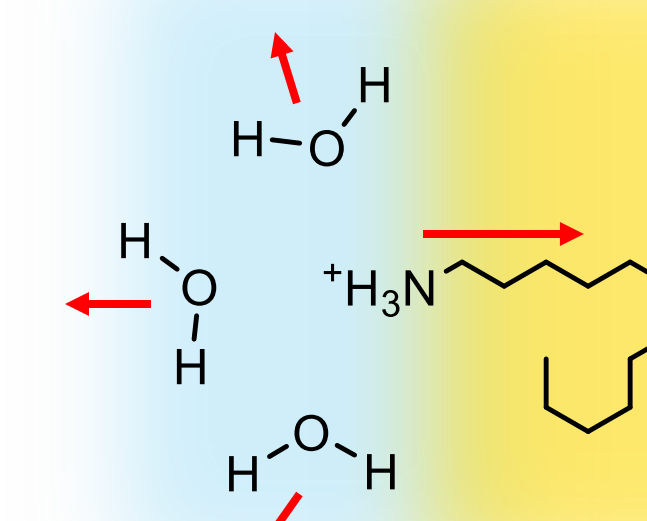
## Low KIE observed for surfactant-like ionophore



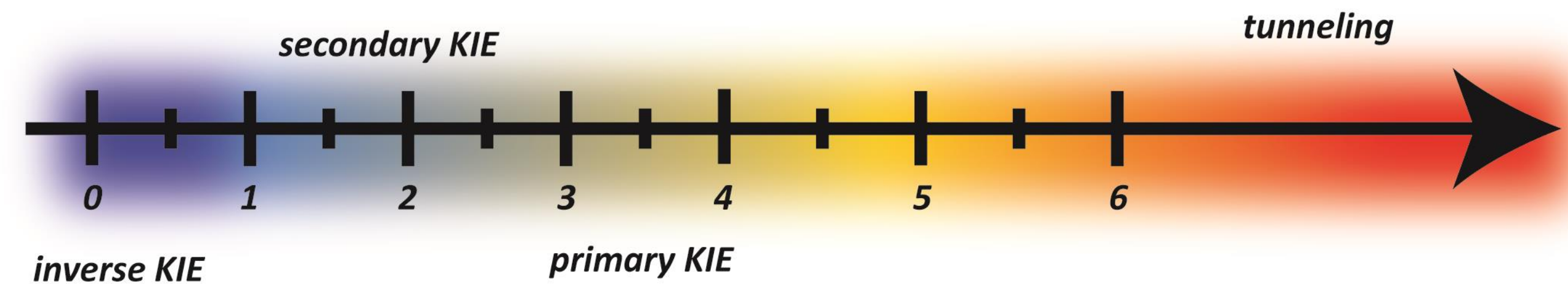
### Data interpretation/mechanistic hypothesis



Direct interfacial proton transfer?

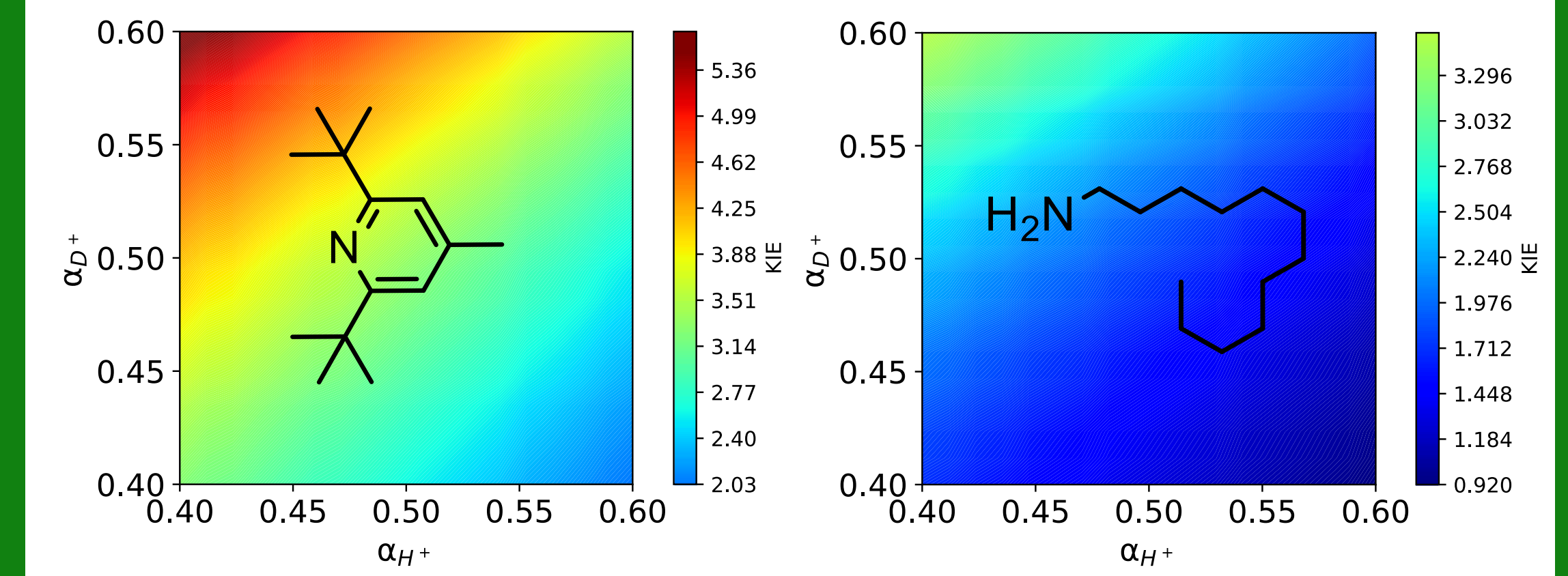


Desolvation/low interfacial diffusion coefficient?



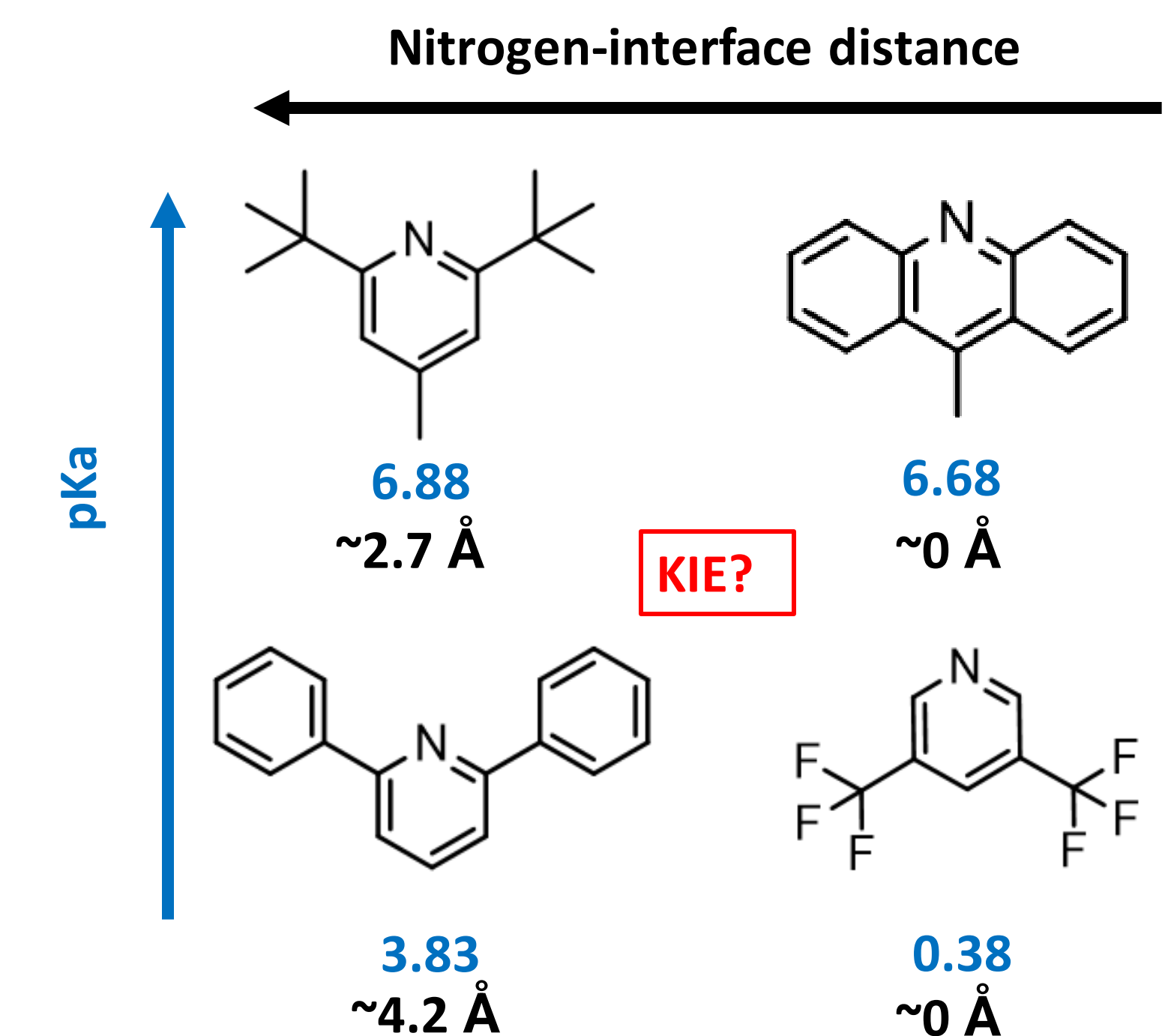
Continuum of KIE values

## KIE - alpha surfaces



- The charge transfer coefficient ( $\alpha$ ) is a parameter in Butler-Volmer formalism for electron transfer kinetics-- often used as a best-fit parameter along with  $k^0$
- This method of comparing relative rate constants is explicitly agnostic of  $\alpha$ , but reveals systematically lower KIE values for the surfactant ionophore for a given combination of possible  $\alpha$ 's

## Future directions



- Hypothesis 1:** KIE will not be a function of ionophore pKa
- Hypothesis 2:** KIE will be proportional to nitrogen-interface separation
- Hypothesis 3:** KIE will be a strong function of ionophore critical micelle concentration (CMC)

## Outlook

- Understanding mechanisms of proton transfer at interfaces is beneficial for energy storage and electrocatalysis
- Our method of determining the KIE of facilitated proton transfer at the ITIES is agnostic of both  $\Delta\phi_o^{0'}$  and  $\alpha$ , both of which are challenging to know apriori for this reaction
- Need to repeat experiment on a variety of ionophores to test which properties influence the KIE measured in this way