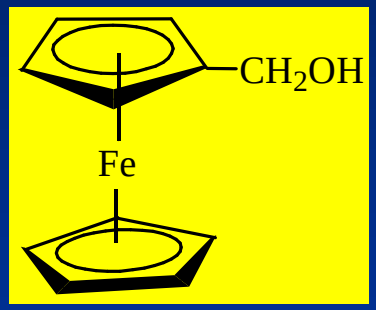
Solution Viscosity Effects on Heterogeneous Kinetics



Electrochemical Active Species: ($FcCH_2OH$)

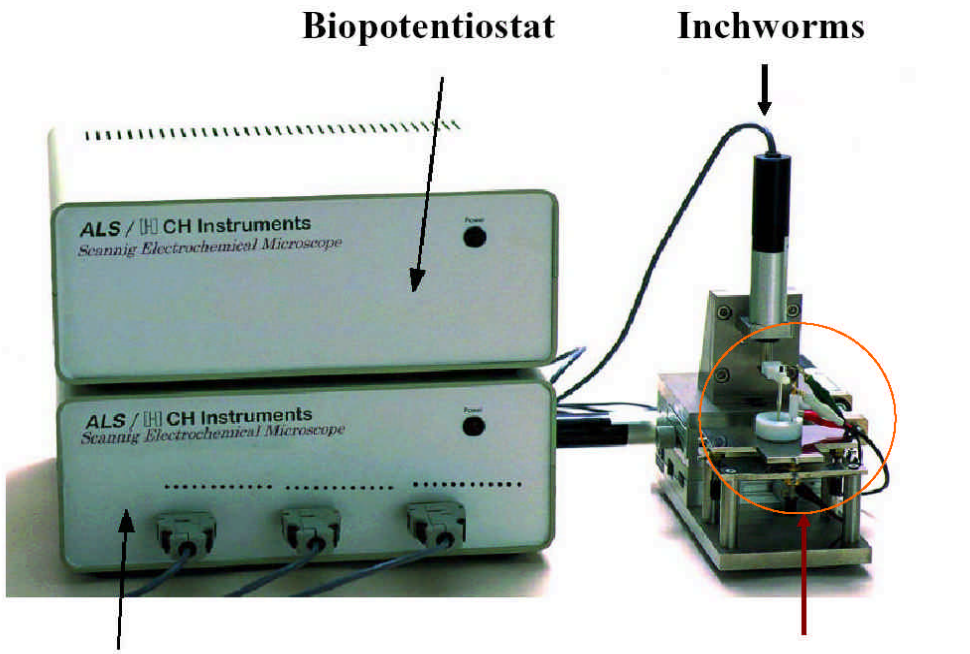
$(CH_3)_2SO$ + H_2O

Solvents (DMSO-Water Mixtures)

$(CH_3)_4NClO_4$

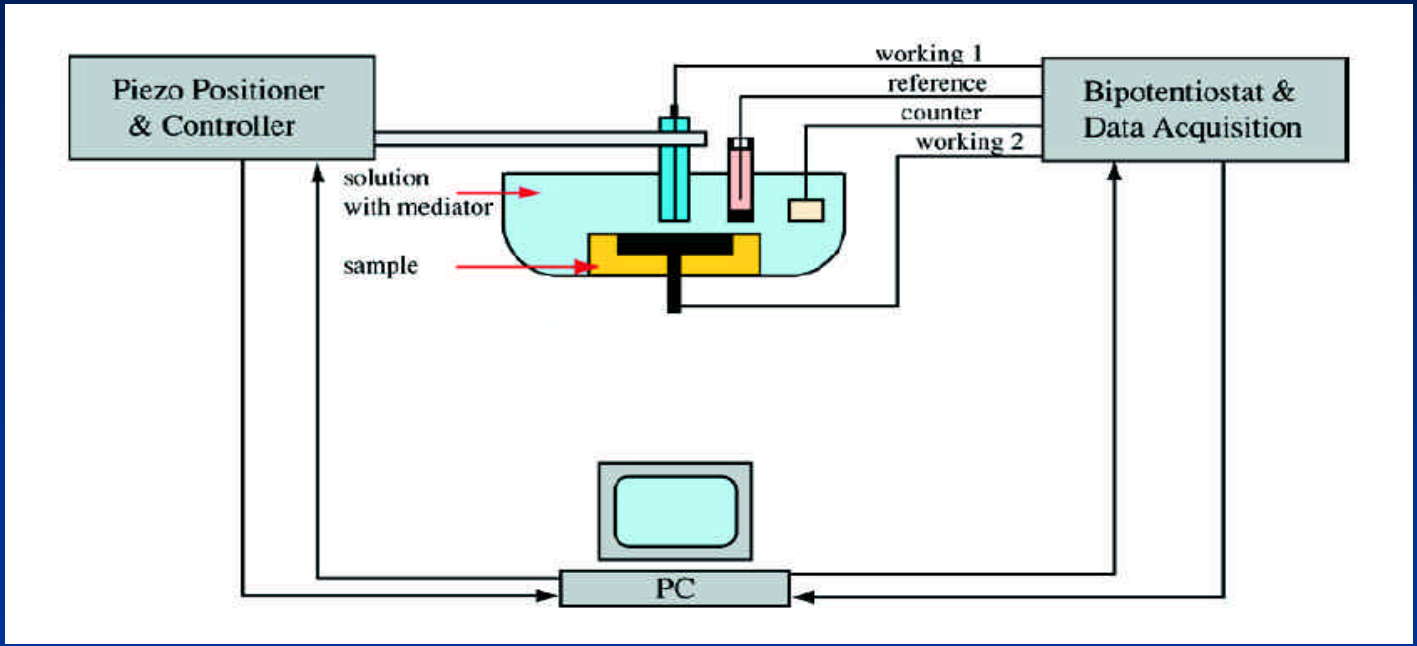
Electrolyte (50mM TMAP)

Experimental Set Up



SECM

Electrochemical Cell Configuration



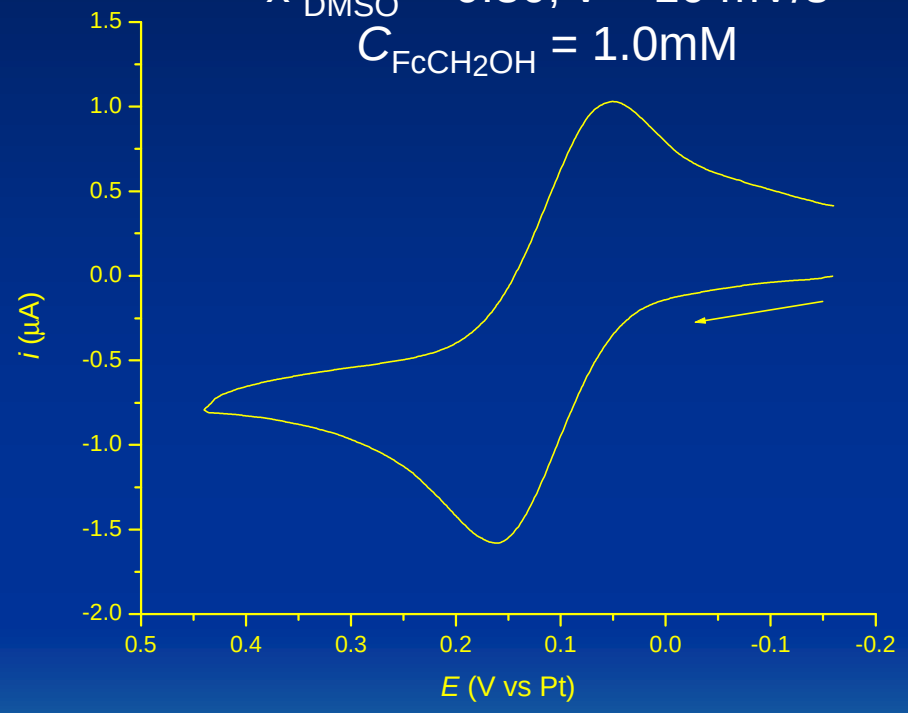
Tip (Working Electrode): 5.06 μm in diameter Pt (R_g ~ 3)

Reference & Counter Electrodes: Pt wire

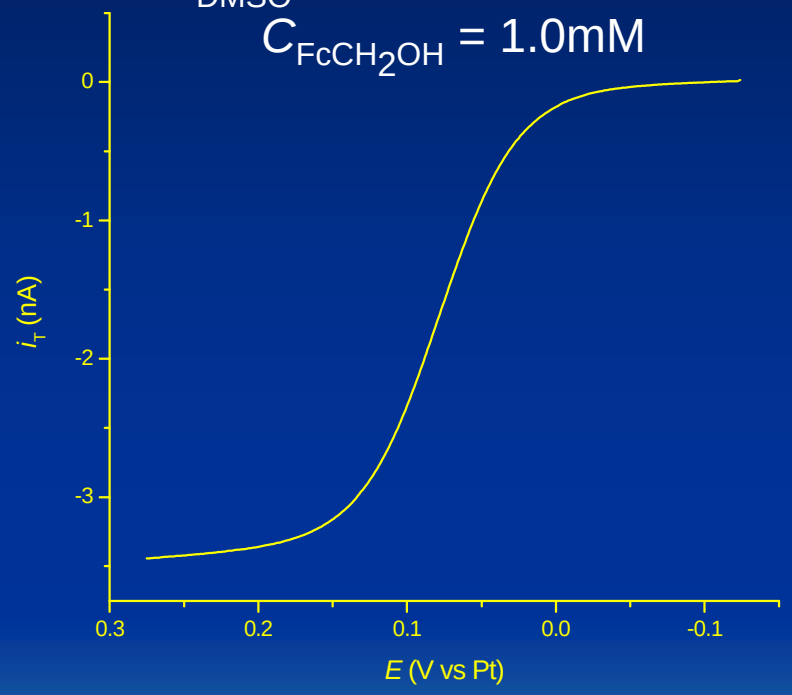
Substrate: 3 mm in diameter Pt disk

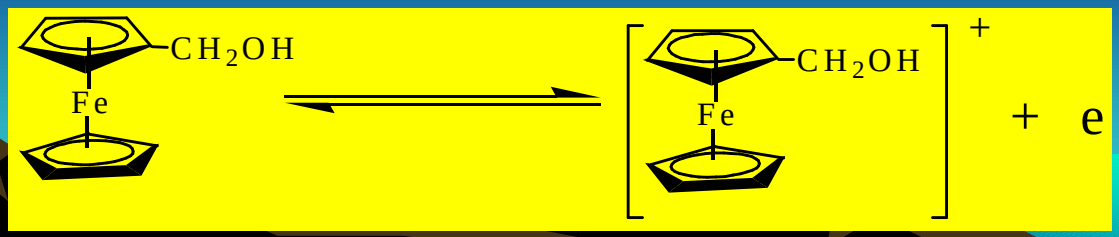
CVs of $FcCH_2OH$ in DMSO-H_2O

At *a* = 1.5 mm Pt
x_{DMSO} = 0.30, v = 10 mV/s
C_{FcCH_2OH} = 1.0mM



At *a* = 2.56 mm Pt
x_{DMSO} = 0.50, v = 20 mV/s
C_{FcCH_2OH} = 1.0mM





Steady-state limiting current

Number of electrons transferred per molecule

Faraday's constant

Bulk concentration

Radius of the tip

$$i_{T,\infty} = 4nFDc^0a$$

Diffusion coefficient

$$D = kT / 6\pi rh$$

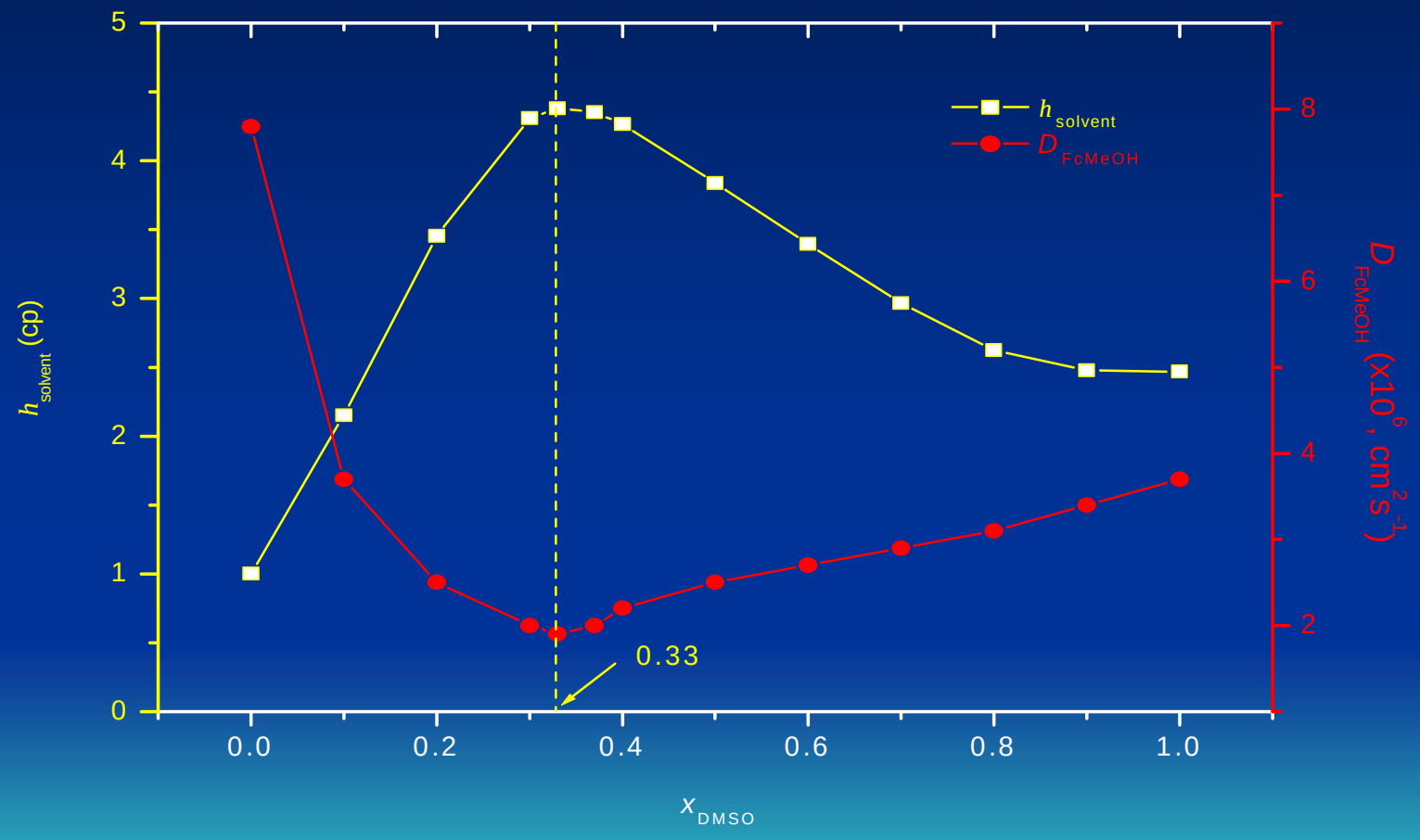
Solution viscosity

Boltzmann's constant

Temperature

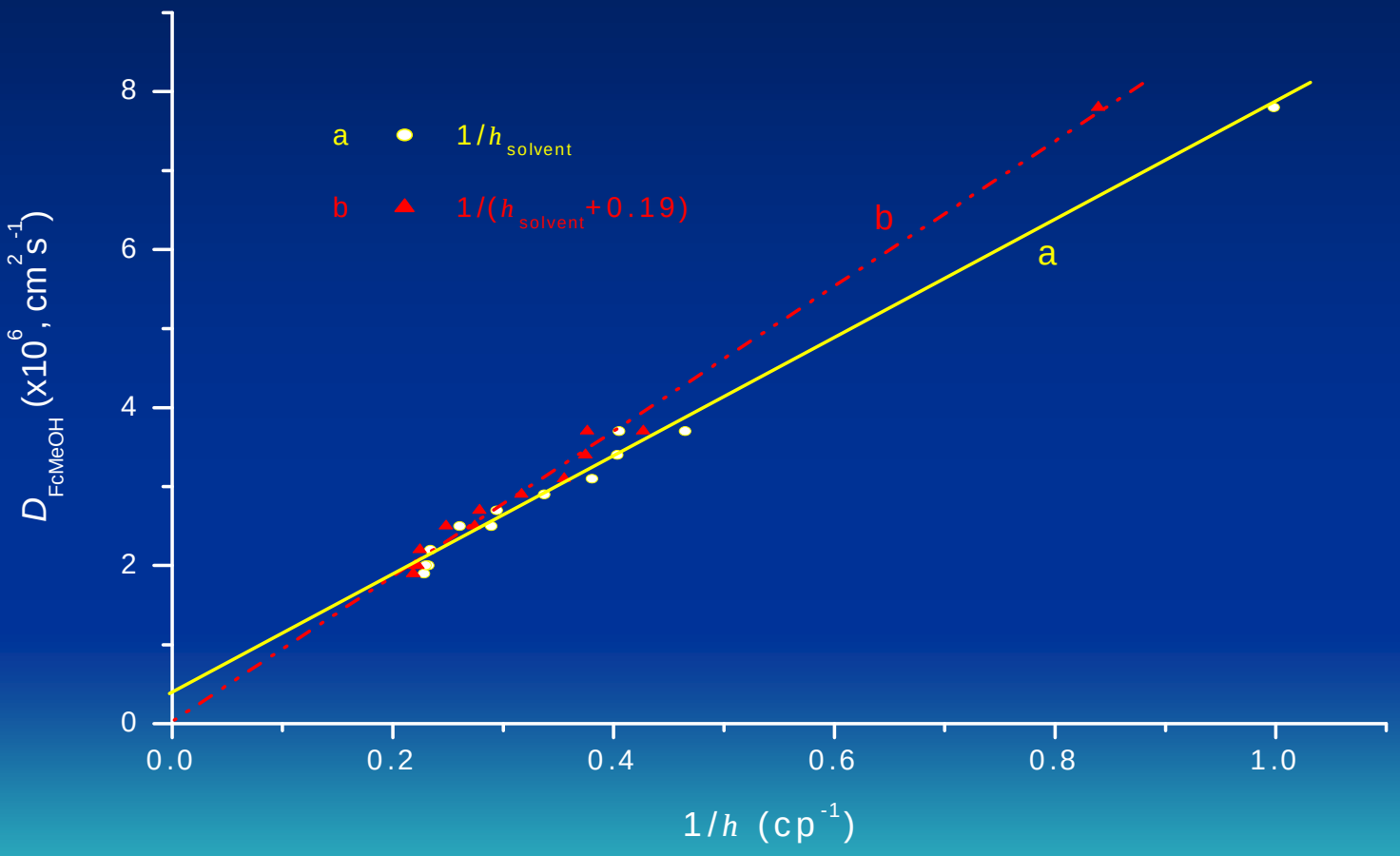
Hydrodynamic radius of the diffusion species

Variations of $h_{solvent}$ and D_{FcCH_2OH} with x_{DMSO}

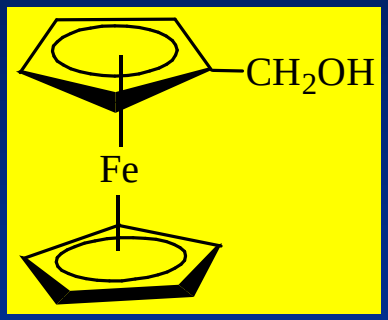


D_{FcCH_2OH} vs. $1/h$

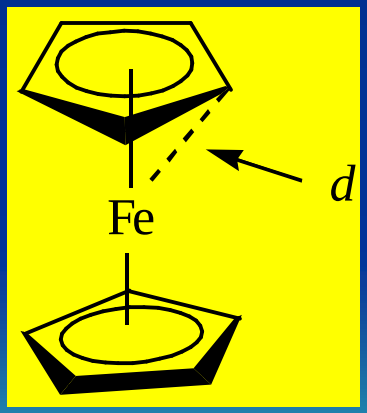
(50 mM TMAP)



Calculation of Hydrodynamic Radius *r*



r = 2.24 Å



$d_{Fe\text{-}C}$= 2.03 Å

Techniques Used to Measure the Heterogeneous ET Rate Constant

- Fast Cyclic Voltammetry
- AC Impedance/Admittance Voltammetry
- Rotating Disk Electrode Measures
- **SECM (Rapid ET rate constant, *iR* Drop)**

SECM Theory for the Measurement of k^0

$$I_T(E,L)/i_{T,\infty} = I_T^C(L)/(q+1/k)$$

$$L = d/a$$

$$I_T^C(L) = i_T/i_{T,\infty}$$

$$q = 1 + \exp[nf(E-E^{0'})]D_O/D_R$$

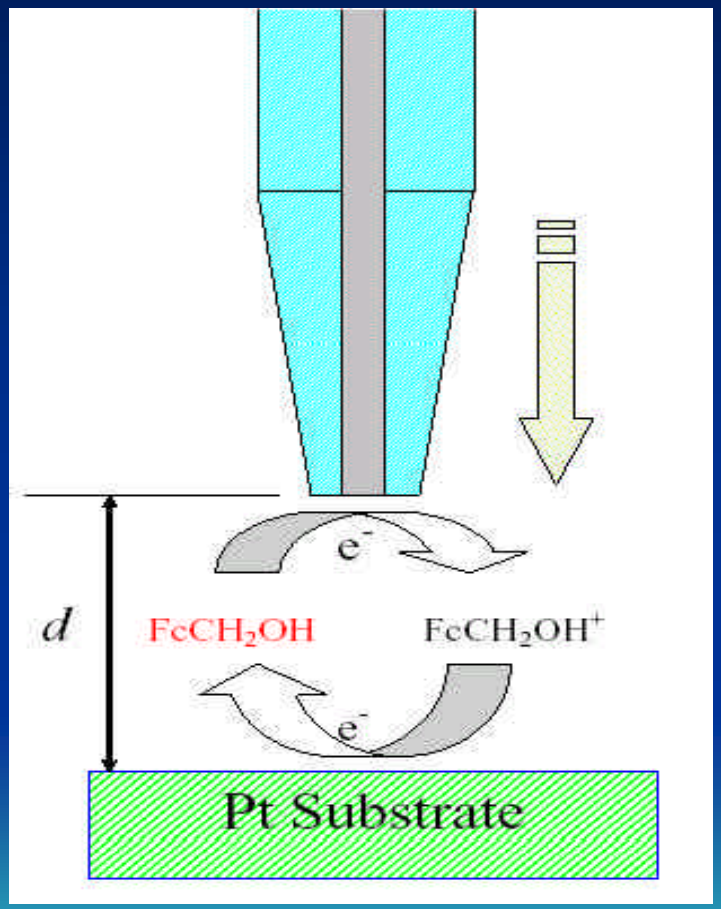
$$k = k^0 \exp[-af(E-E^{0'})m_0$$

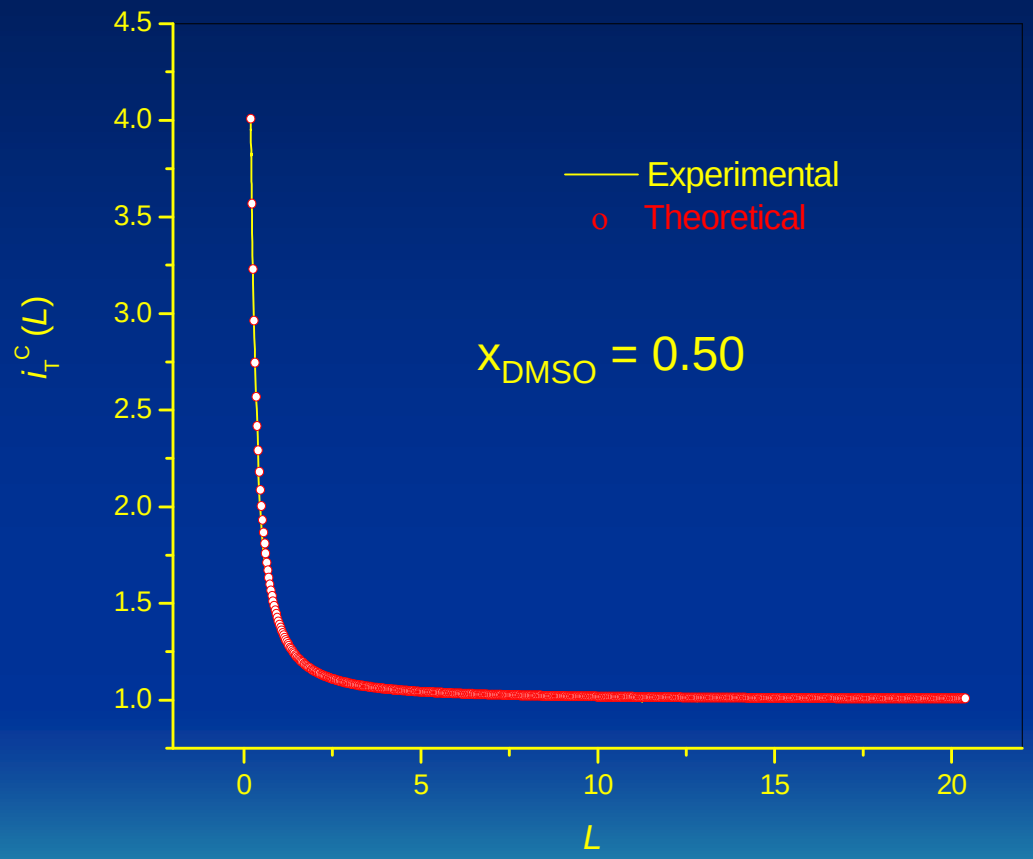
Effective Mass Transfer Coefficient

$$m_0 = 4D_o I_T^C(L)/pa$$

$$f = F/RT$$

Tip Approach Curve Fitting



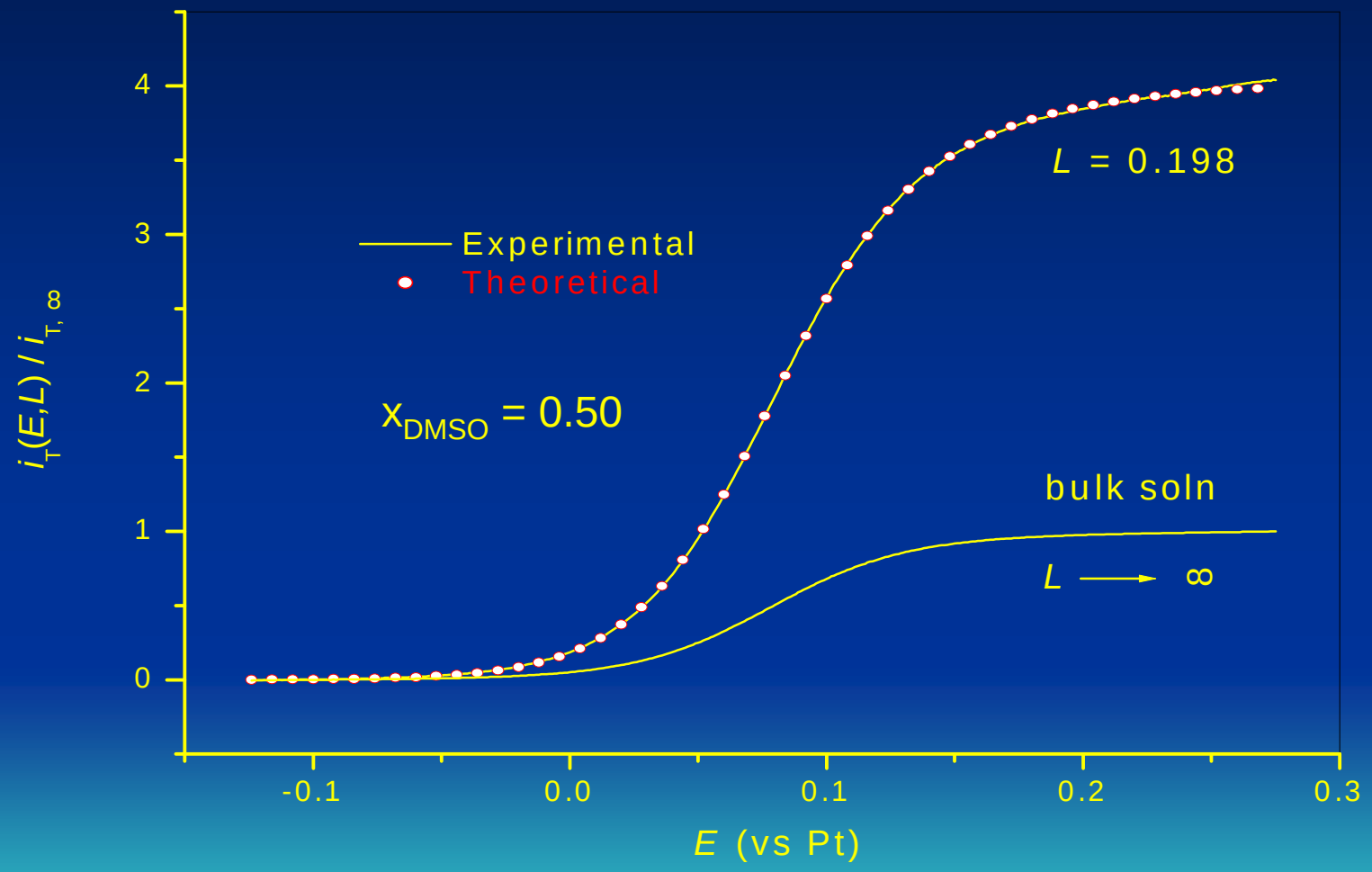


$$I_T^C(L) = k_1 + k_2 / L + k_3 \exp(k_4 / L)$$

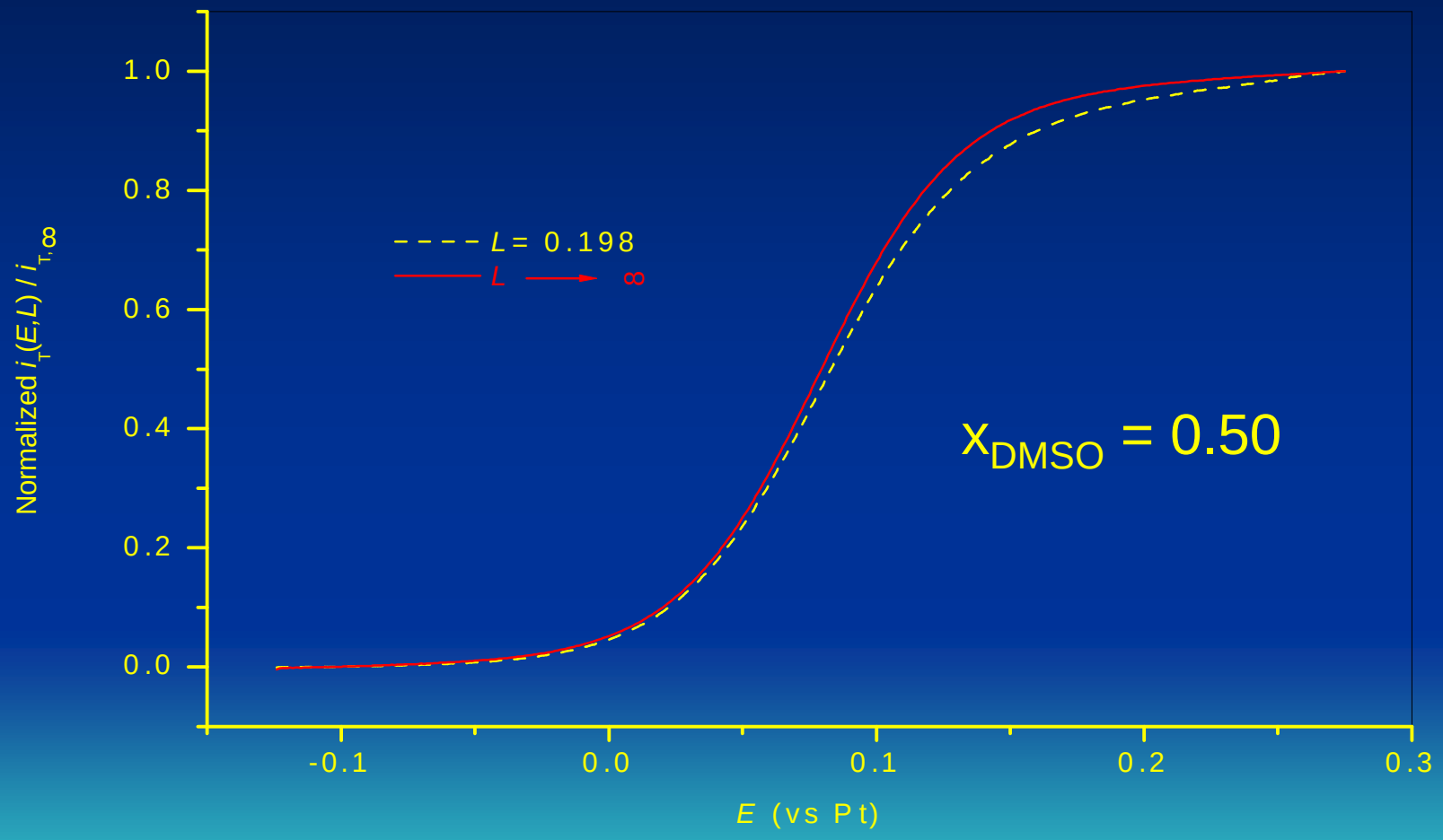
E_{tip} = 0.35 V, E_S = -0.15 V vs Pt

k_1 = 0.63349, k_2 = 0.67476, k_3 = 0.36509 and k_4 = -1.42897

Tip Voltammogram Fitting



Normalized Tip Voltammograms at Different *L* Values

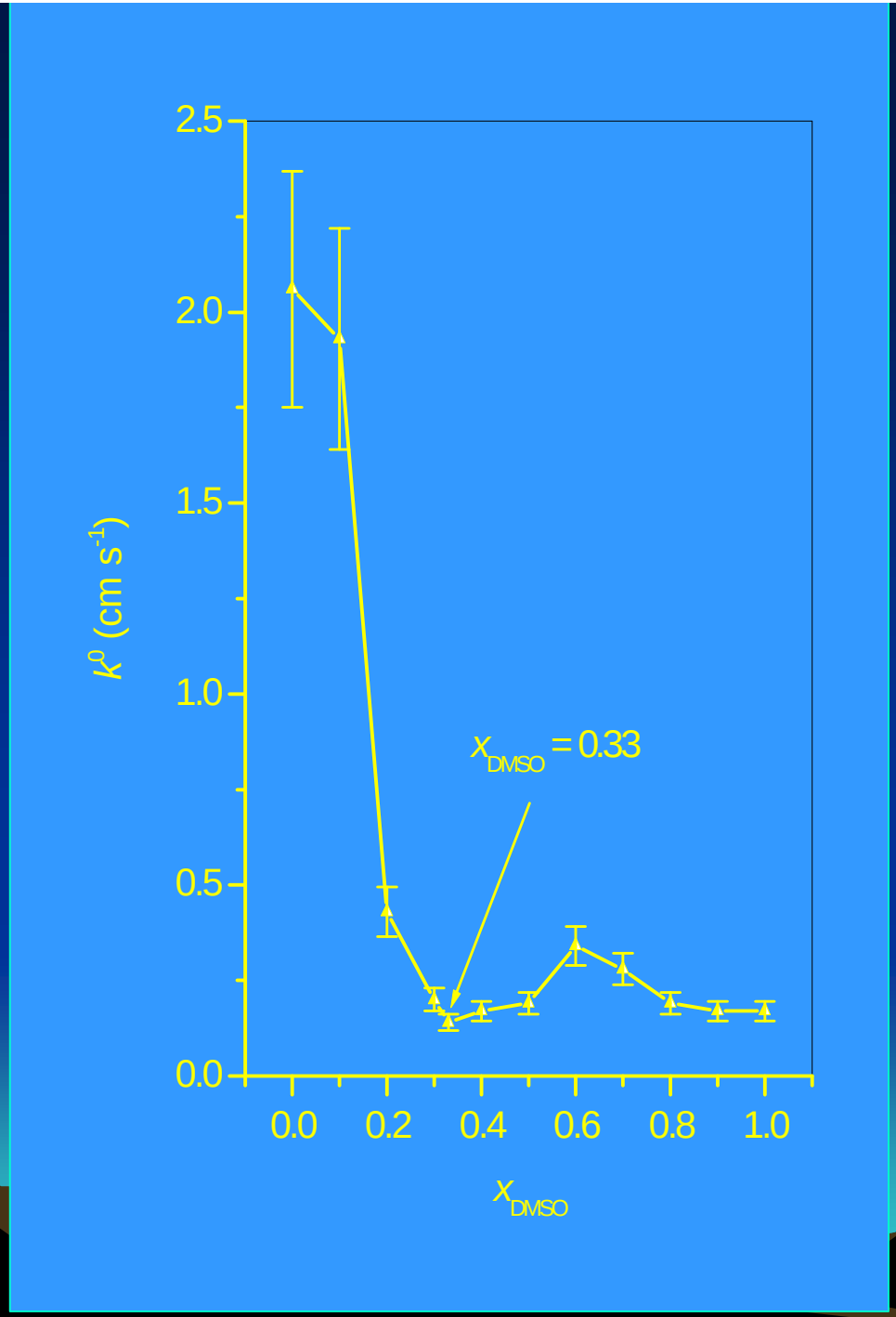


Kinetic Parameters for $FcCH_2OH$-DMSO/H_2O System (1)

x_{DMSO}	h (cp)[a] (±0.55%)	D ($\times 10^6$, $cm^2\ s^{-1}$, ±3%)	I_T^C (L)	L	m_0 ($\times 10^2$, $cm\ s^{-1}$)
0	1.002[b]	7.8	3.95	0.204	15.51
0.10	2.152	3.7	4.00	0.200	7.452
0.20	3.455	2.5	3.99	0.201	5.022
0.30	4.31	2.0	4.06	0.197	4.088
0.33	4.383	1.9	4.02	0.199	3.845
0.37	4.354[c]	2.0			
0.40	4.267	2.2	3.93	0.205	4.353
0.50	3.838	2.5	4.04	0.198	5.085
0.60	3.398	2.7	4.03	0.199	5.479
0.70	2.967	2.9	3.99	0.201	5.826
0.80	2.627	3.1	4.05	0.198	6.320
0.90	2.478[c]	3.4	4.01	0.200	6.866
1.00	2.47[d]	3.7	3.94	0.204	7.340

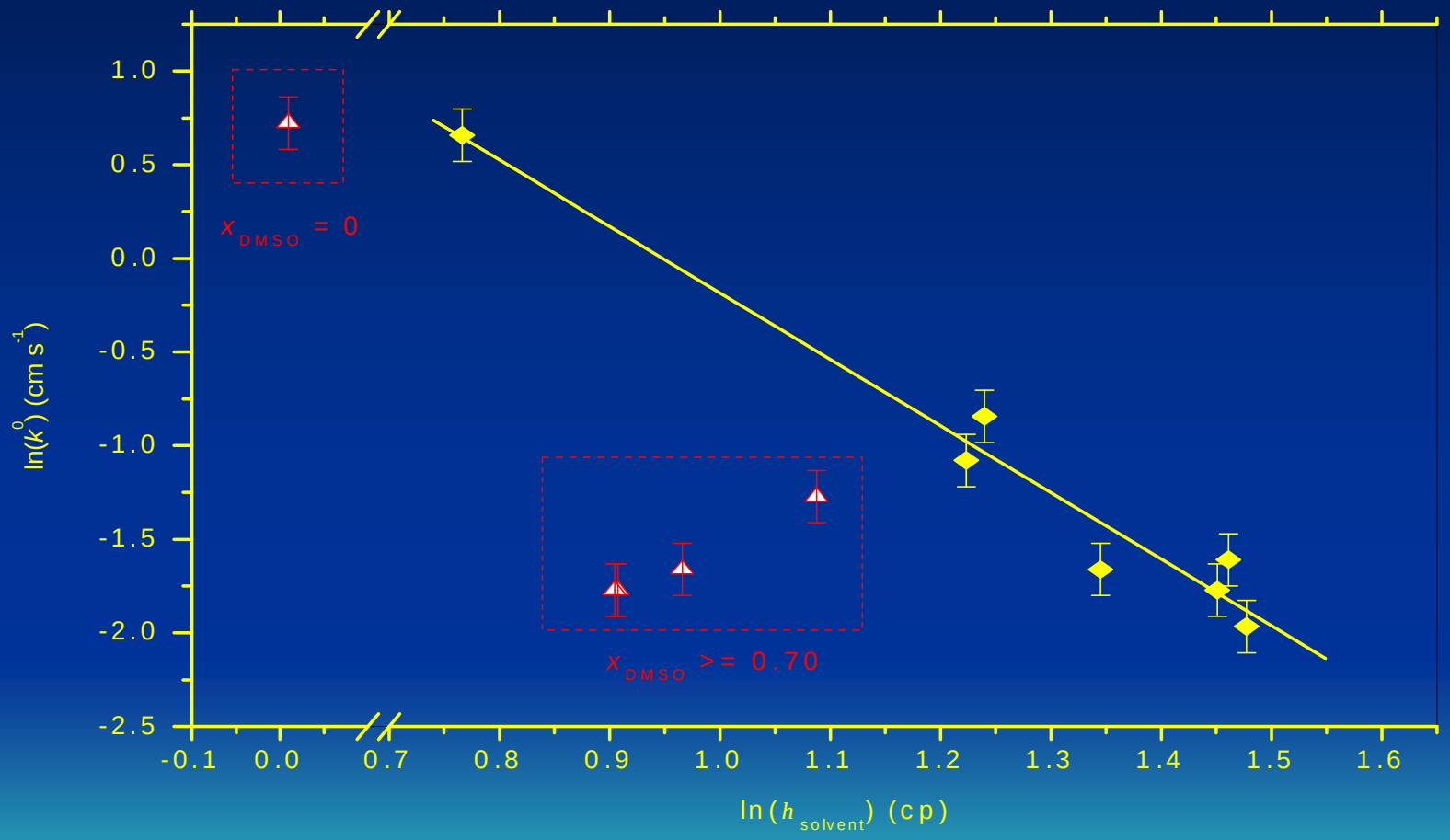
Kinetic Parameters for $FcCH_2OH$-DMSO/H_2O System (2)

x_{DMSO}	k^0 (cm s^{-1} ±5%)	$E^{0'}$ (mV vs Pt, ±3 mV)	α (±0.02)
0	2.06	48	0.20
0.10	1.93	50	0.19
0.20	0.43	70	0.32
0.30	0.20	75	0.31
0.33	0.14	71	0.36
0.37			
0.40	0.17	79	0.40
0.50	0.19	80	0.40
0.60	0.34	86	0.34
0.70	0.28	81	0.32
0.80	0.19	91	0.33
0.90	0.17	94	0.35
1.00	0.17	160	0.36



ET Rate Constants vs x_{DMSO}

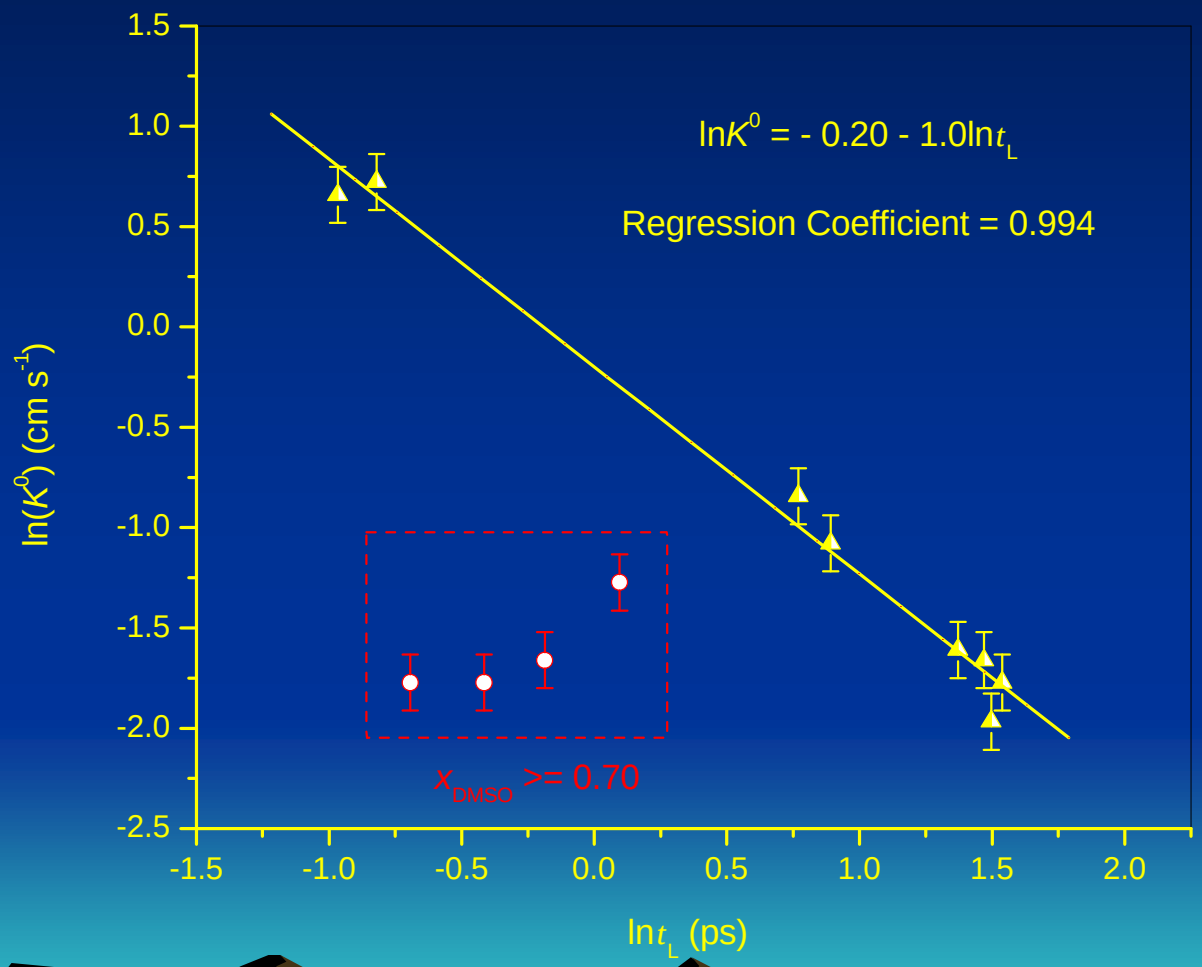
Correlation Between $\ln k^0$ and $\ln h_{solvent}$



$\ln k^0 = 3.37 - 3.55 \ln h_{solvent}$ (regression coefficient = 0.983)

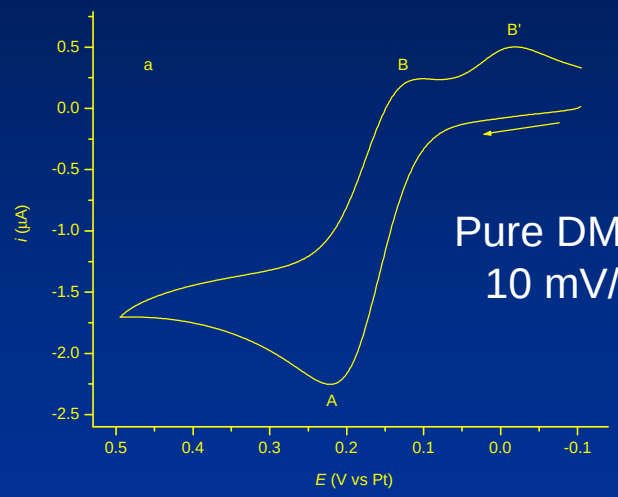
Correlation Between $\ln k^0$ and $\ln \tau_L$*

x_{DMSO}	τ_L (ps)[e]
0	0.44[f]
0.10	0.38
0.20	2.16
0.30	3.94
0.33	4.47
0.37	
0.40	4.66
0.50	4.35
0.60	2.44
0.70	1.10
0.80	0.83
0.90	0.66
1.00	0.50

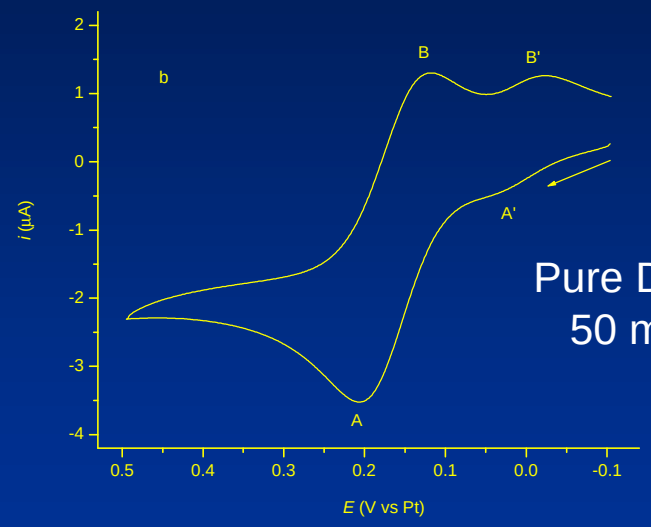


* τ_L—longitudinal Relaxation Time

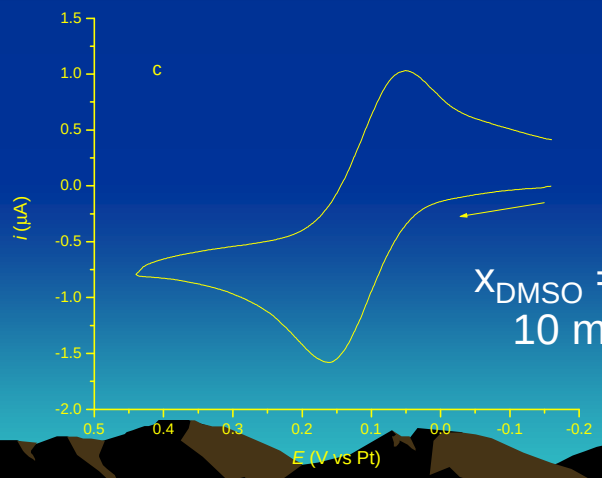
Influence of Adsorption on k^0 When x_{DMSO} = 0.70



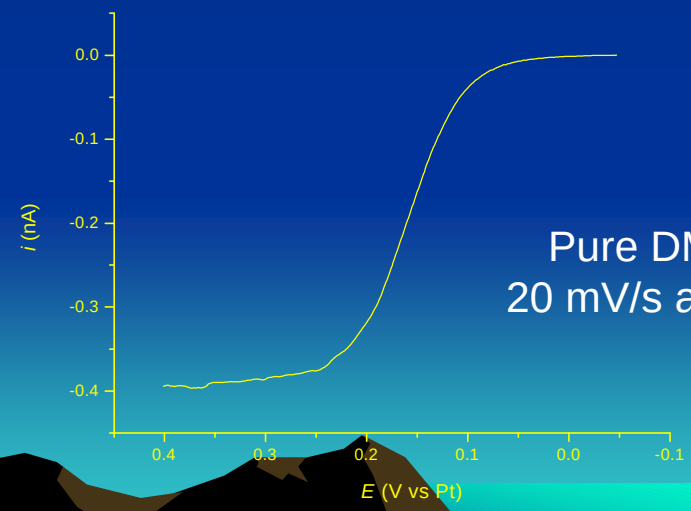
Pure DMSO
10 mV/s



Pure DMSO
50 mV/s



x_{DMSO} = 0.30
10 mV/S



Pure DMSO
20 mV/s at Pt tip

(a) To (c) at 3 mm Pt electrode

Conclusions

$$k^0_{\max} = 2.06 \pm 0.31 \text{cm/s (pure water)}$$

$$k^0_{\min} = 0.14 \pm 0.02 \text{cm/s } (x_{DMSO} = 0.33)$$

$$\ln k^0 \propto \ln h$$

$$\ln k^0 \propto \ln t_L$$

Adsorption $(x_{DMSO} \geq 0.70)$