Electrokinetic/Surfactant-Enhanced Removal of Hydrophobic Organic Contaminants (HOCs) in Subsurface Environments

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Background

- Hydrophobic Organic Contaminants (HOCs)
  - Widespread presence in the environment
  - High toxicity (mutagenic and/or carcinogenic)
  - Persistent in the environment
- HOCs in Subsurface Environments
  - High affinity to solid phase
  - Slow dissolution/desorption rate
  - Inaccessibility of removal agents through fine soils

  ➔ No in-situ remediation technologies

Objectives

- Combination of
  - Enhanced HOC solubilization/desorption
  - Accelerated HOC transport from fine soils
- Goals
  - To evaluate the electrokinetic/surfactant removal of HOC from fine soil
- Considerations:
  - Effects of surfactant (micelles and sorbed surfactant) on EK properties of fine soil
  - Effect of EK on surfactant sorption and HOC partitioning

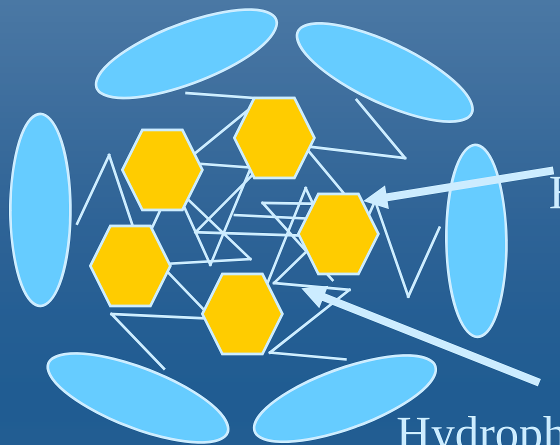
Methodology

- Experiments
  - Batch and column experiments
  - HOCs: Naphthalene and Phenanthrene
  - Surfactants: SDS, Tween 80, and Hydroxypropyl-β-cyclodextrin (HPCD)
  - Soil mineral: Kaolinite
- Numerical Model
  - 1-D Finite difference method (FDM)
  - Two components (HOC and surfactant) in three phases (water, micelle, solid) - kinetic model

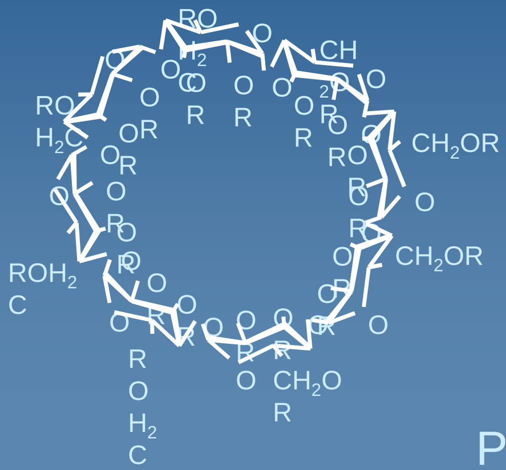
SER of HOCs in Soil

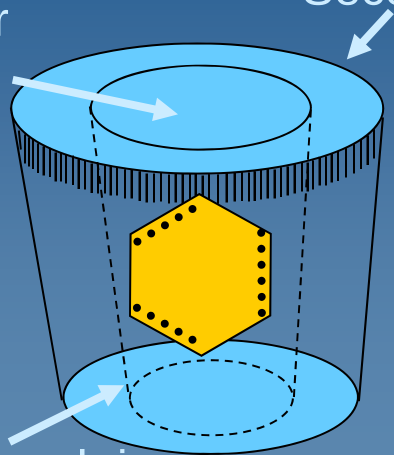
- Surfactant?

Surfactant micelle

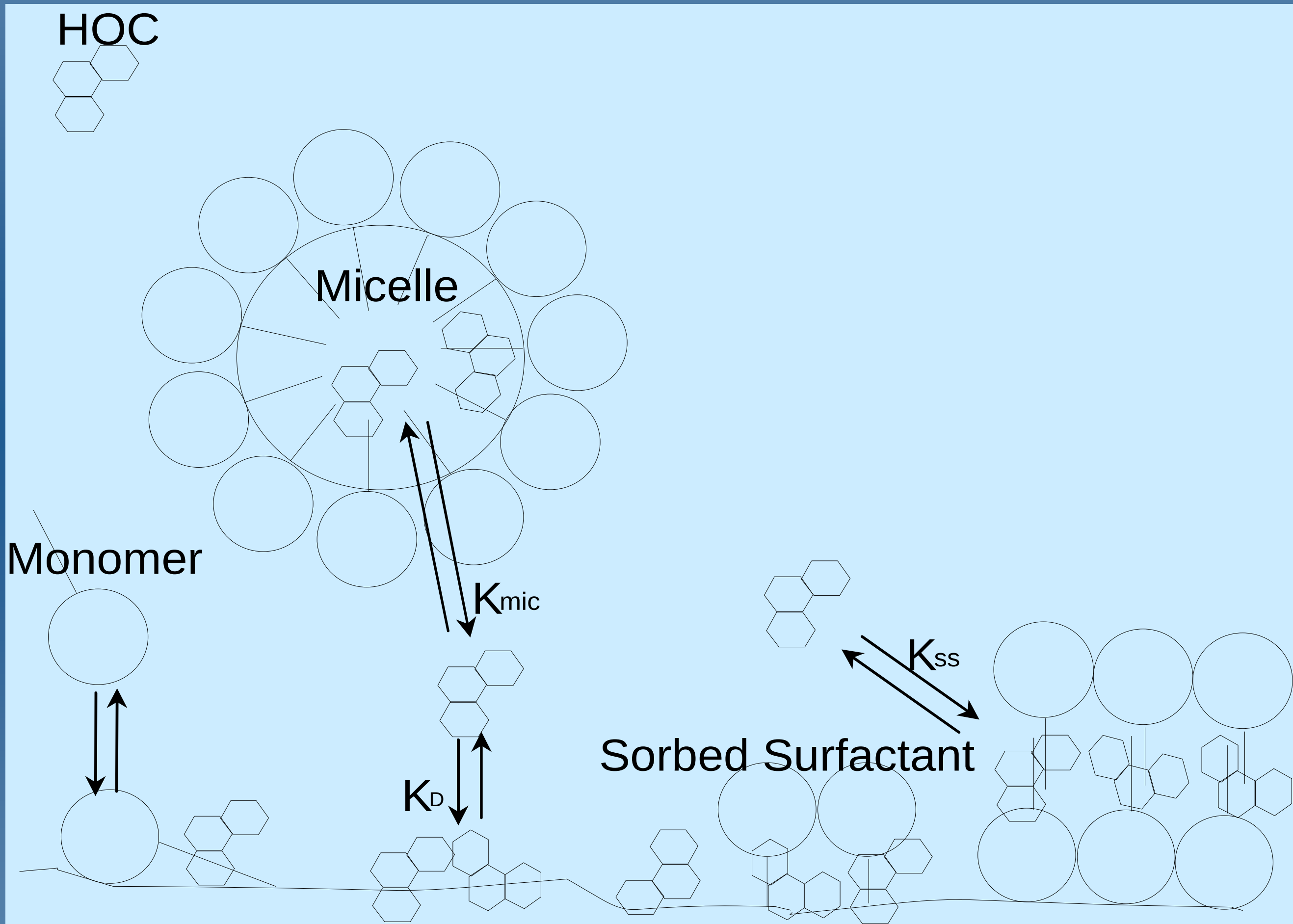


Beta-Cyclodextrin





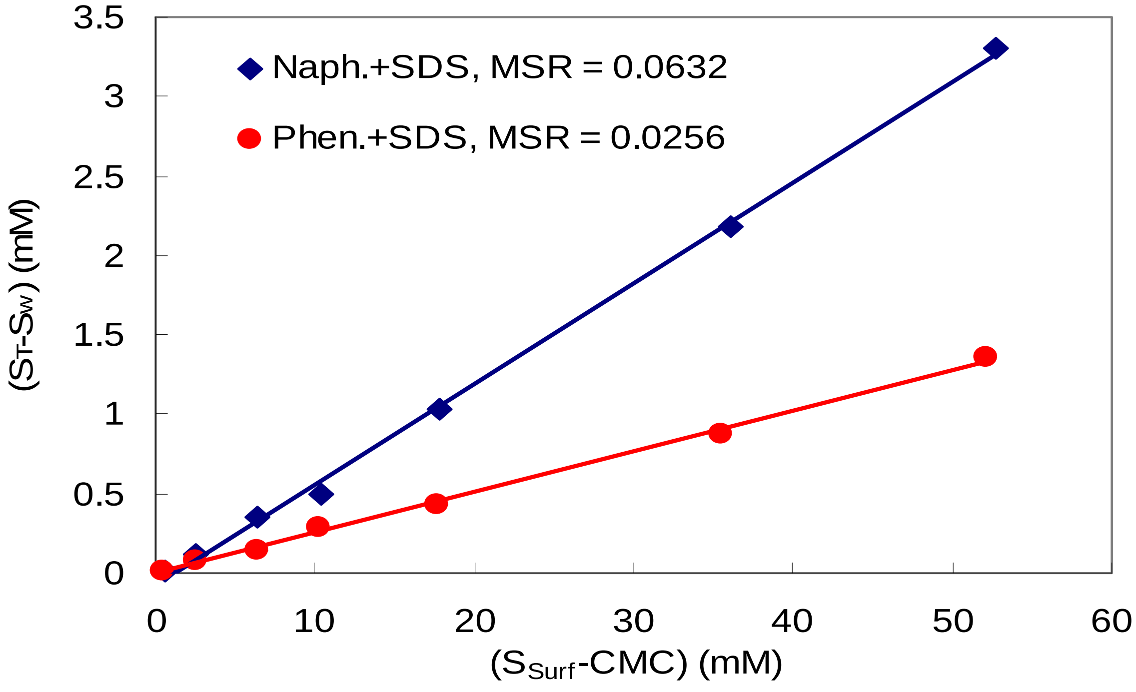
Surfactants in HOCs contaminated subsurface



- $K_{min(D)}$, K_{mic}, K_{ss} = $f\,(C_{HOC}, S_{surf}, pH, I)$

Micellar Partition Coefficient (K_{mic})

- Solubility Enhancement Method

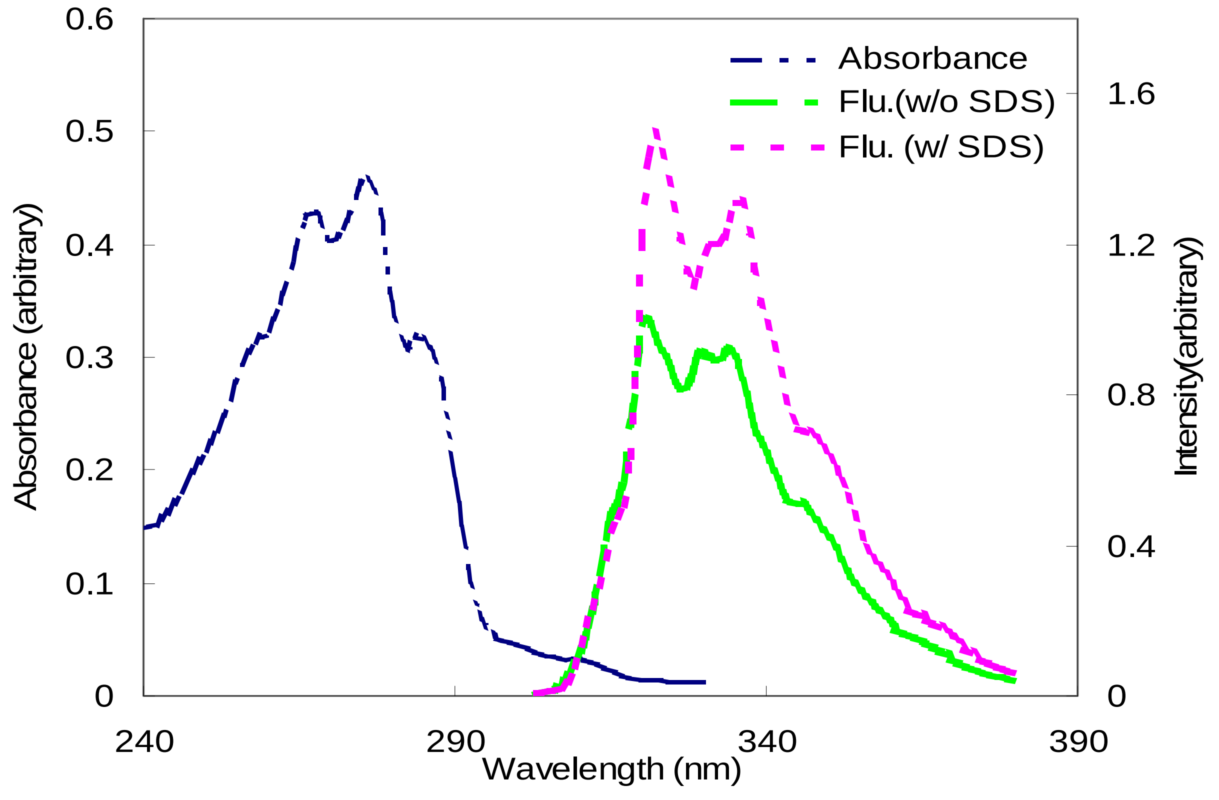


Enhanced Solubility of Naphthalene and Phenanthrene by SDS

➔only measure the saturation limit

◇ *Micellar Partition Coefficient (K_{mic})*

- Fluorescence technique

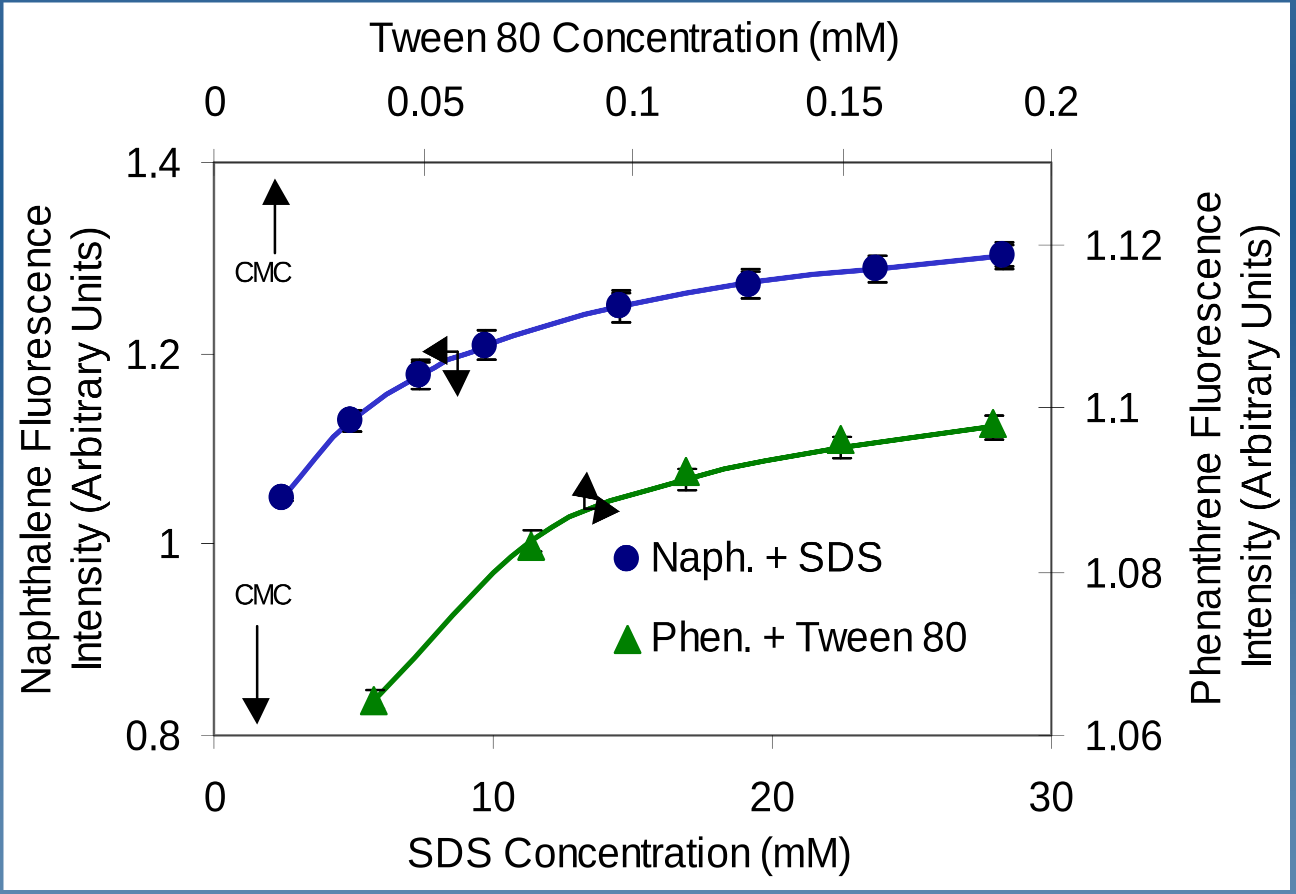


Absorption/Emission Spectra of Naphthalene

- can obtain K_{mic}s as a function of C_{HOCs}

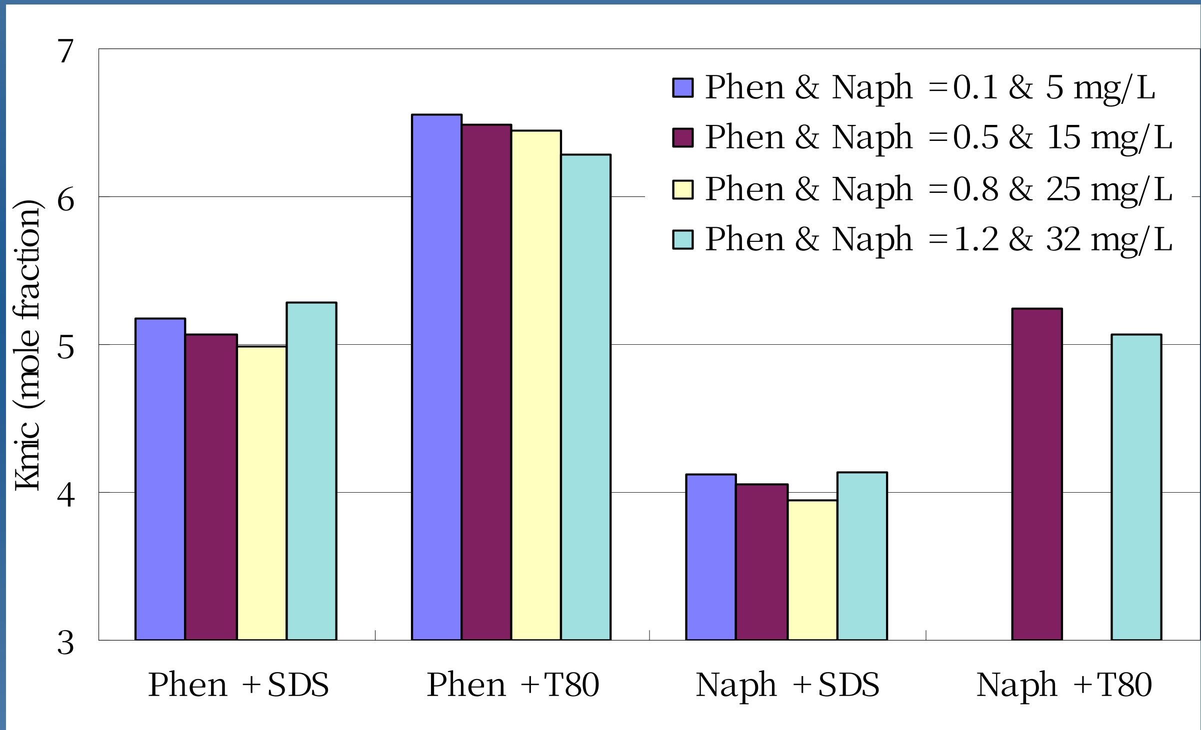
Micellar Partition Coefficient (K_{mic})

$$F_t = \frac{F_w + F_{mic} \cdot K_{mic} \cdot (S_{surf} - CMC)}{1 + K_{mic} \cdot (S_{surf} - CMC)}$$



Micellar Partition Coefficient (K_{mic})

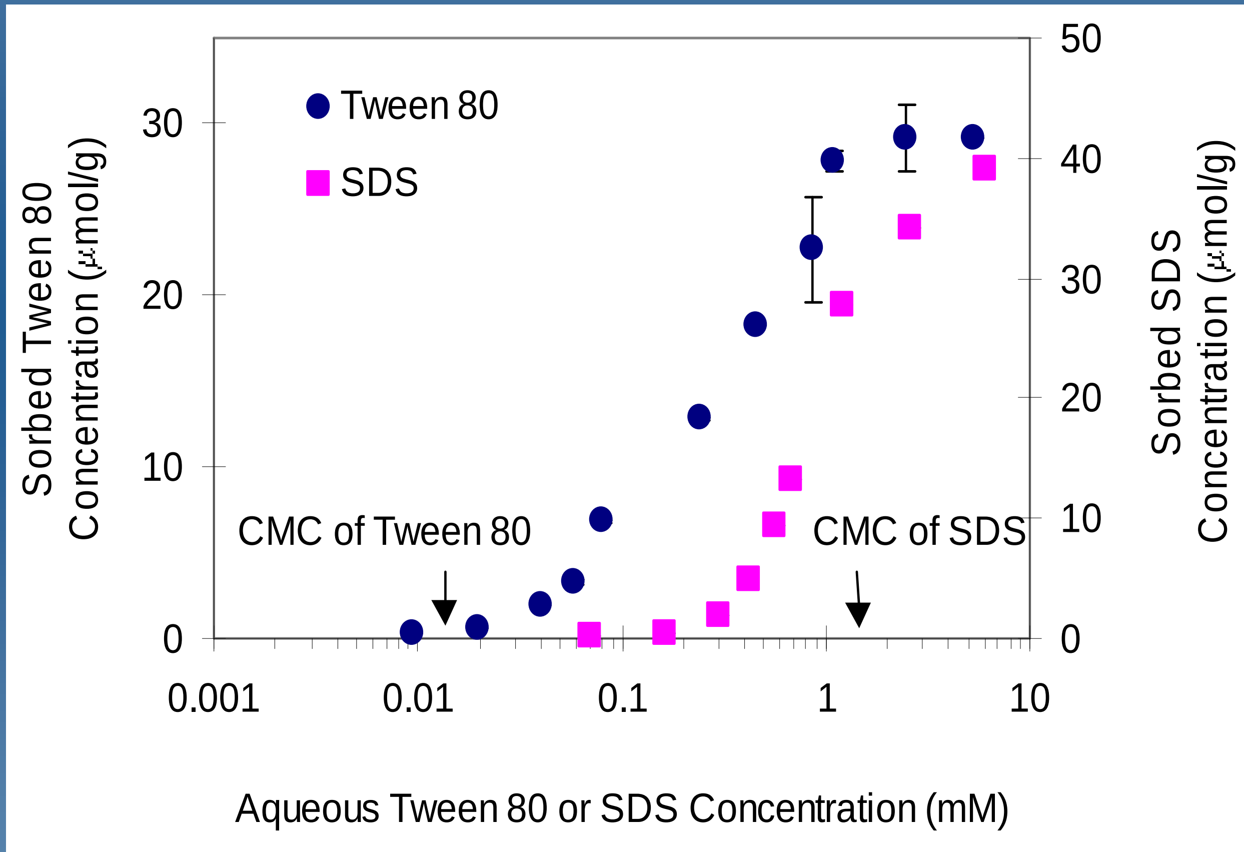
- K_{mic}s



- Two-site model
- K_{mic} = f (HOC type, HOC conc.)

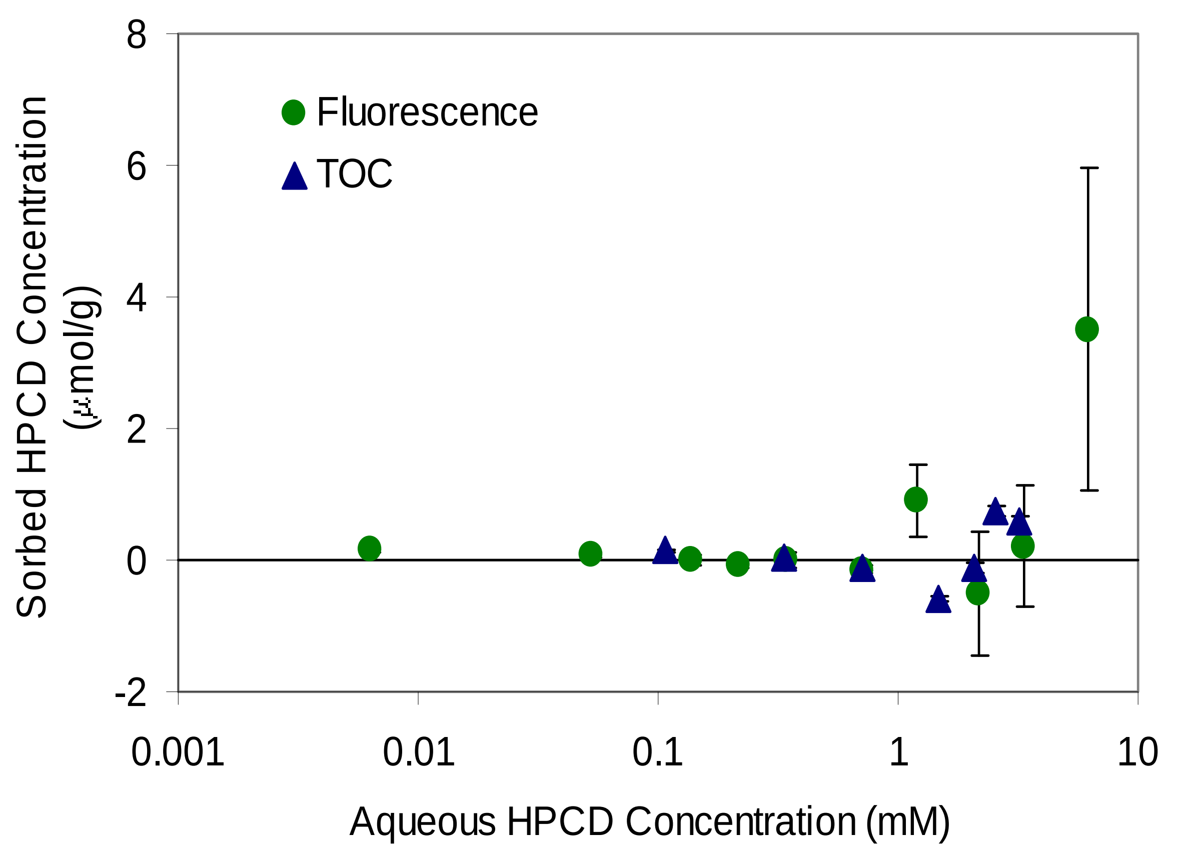
Surfactant Sorption on Kaolinite

- Sorption isotherms



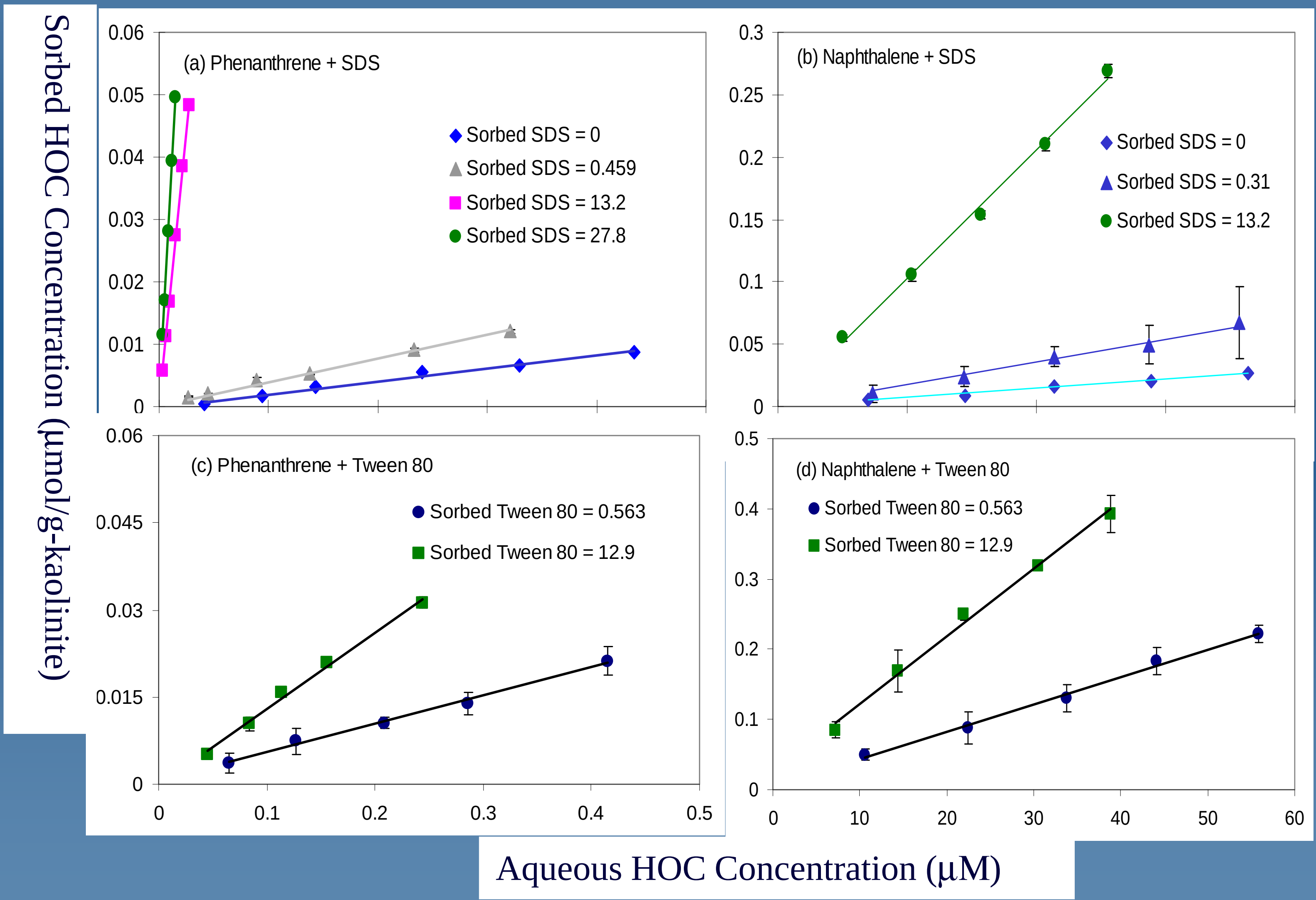
Surfactant Sorption on Kaolinite

- HPCD sorption isotherms



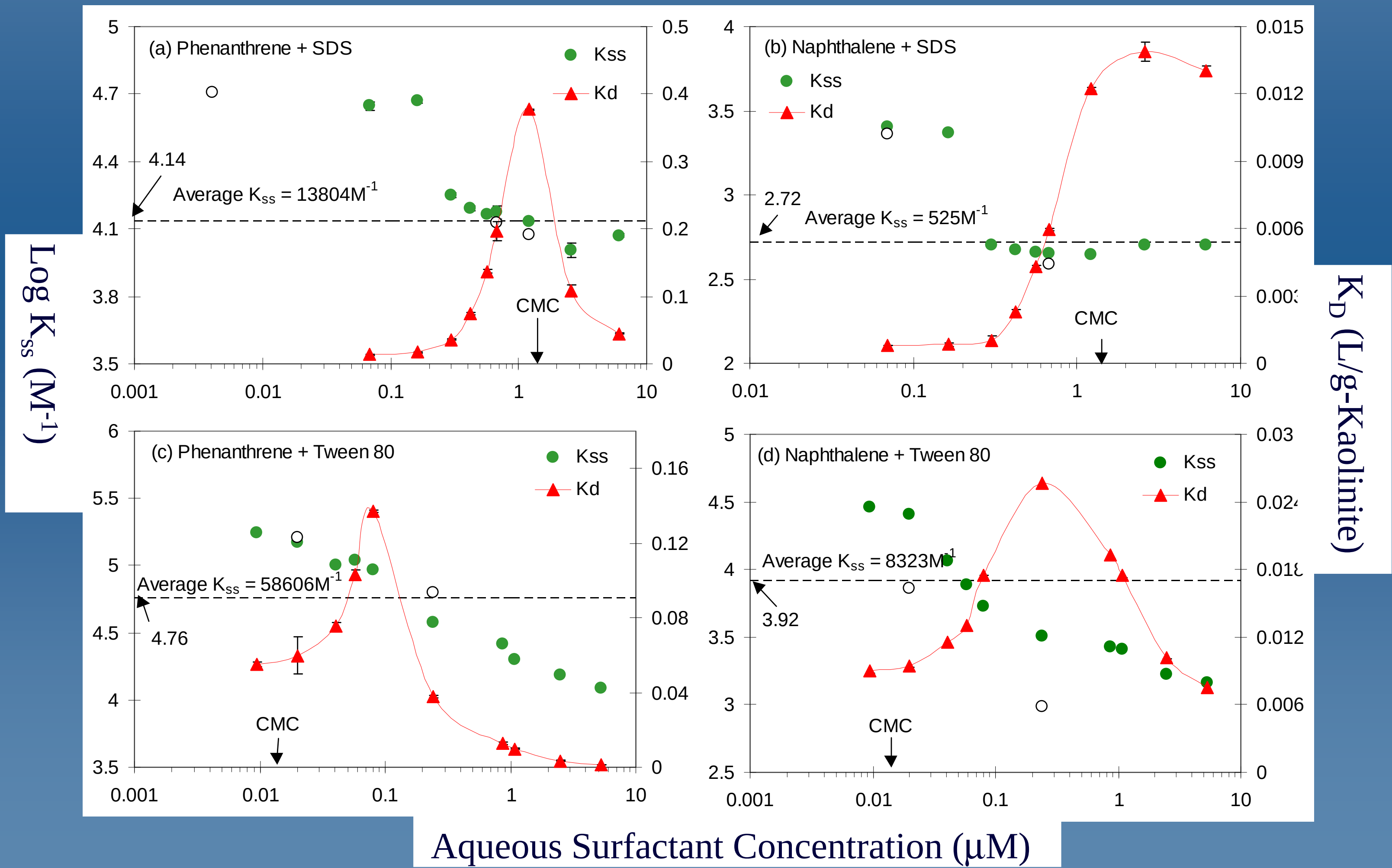
HOC Partitioning to Sorbed Surfactant

- HOC sorption isotherms (K_D)



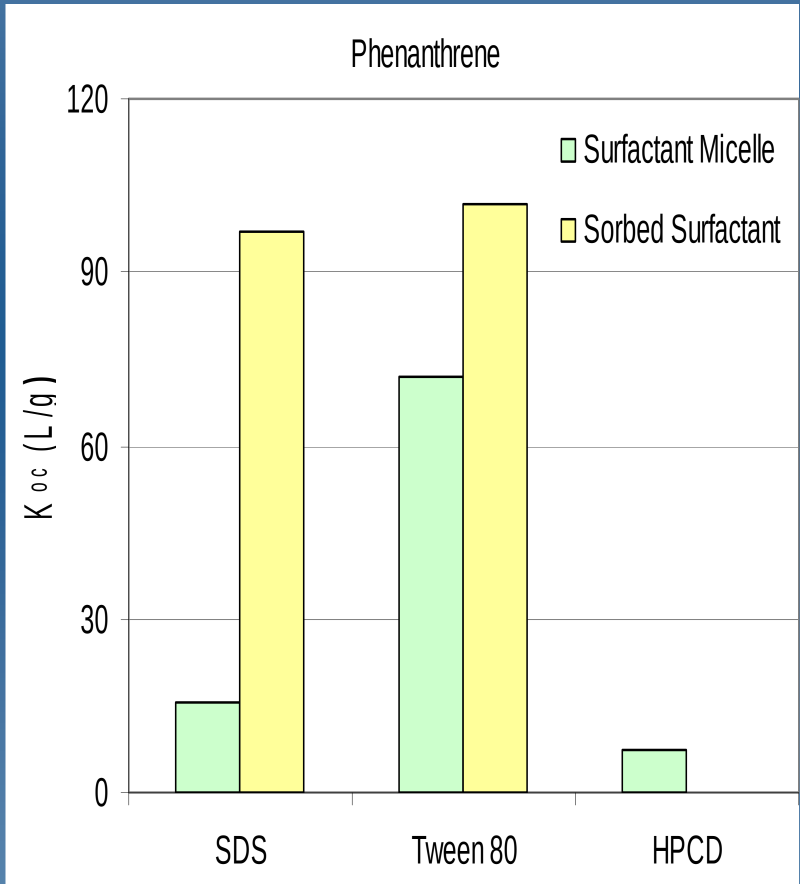
HOC Partitioning to Sorbed Surfactant

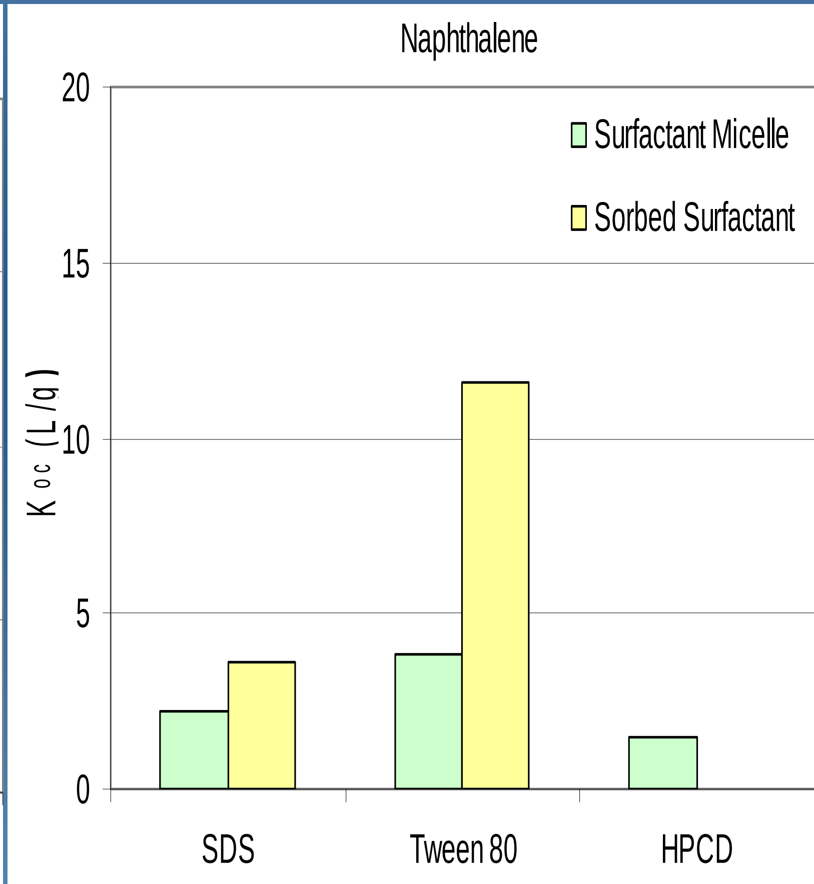
$$K_D = \frac{C_{immob}}{C_{mob}} = \frac{S_{sorb} \cdot K_{ss} + K_{\min}}{1 + K_{mic} \cdot (S_{surf} - CMC)}$$



Summary of HOC Partitioning Coeff.

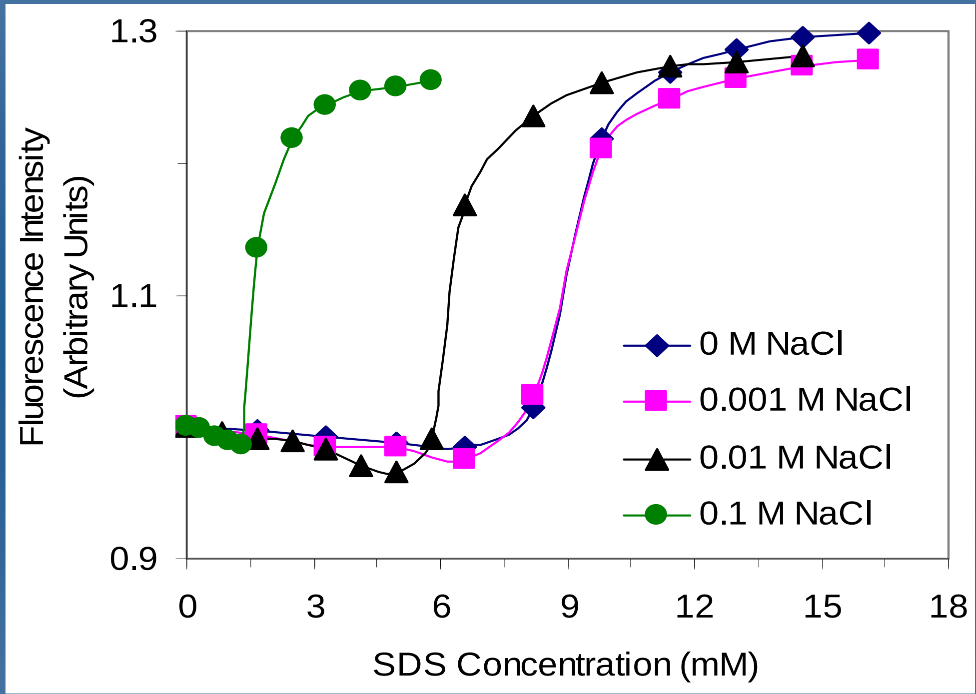
- K_{mic} and K_{ss} (K_{oc} basis)





Solution Chemistry Effects on SER

- CMC

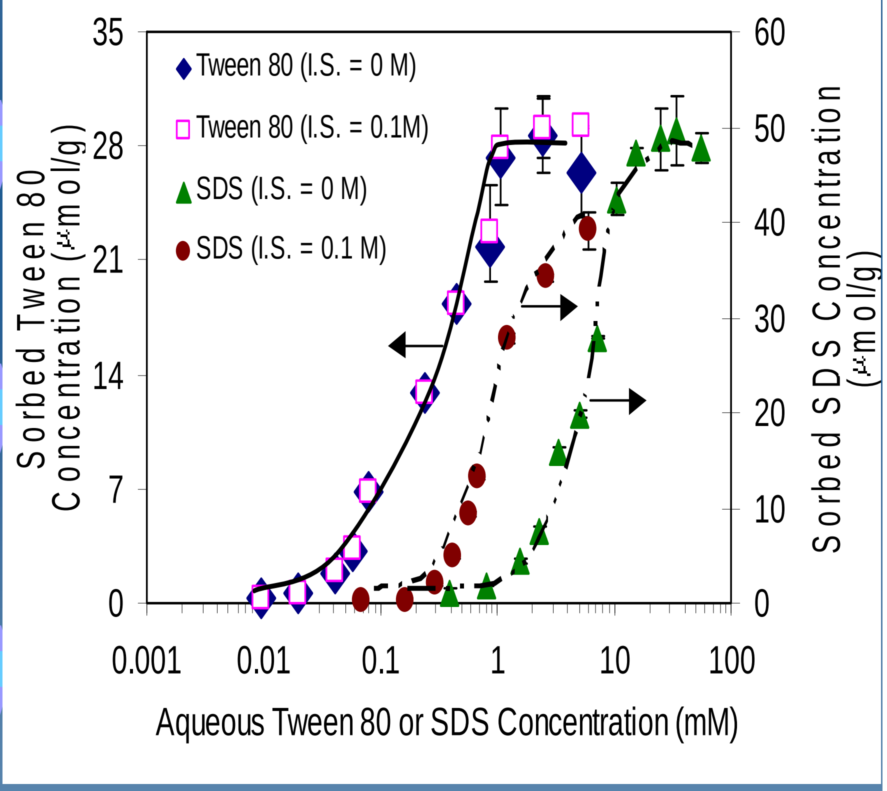


- K_{mic} for SDS - only affected by Ionic strength

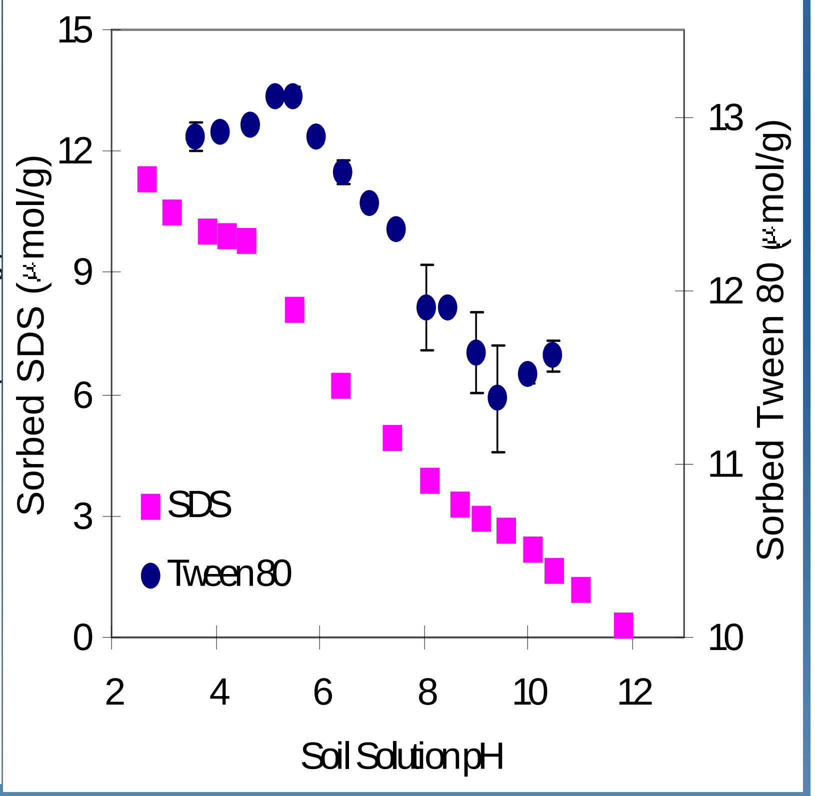
Solution Chemistry Effects on SER

- Surfactant sorption

<Ionic strength effects>



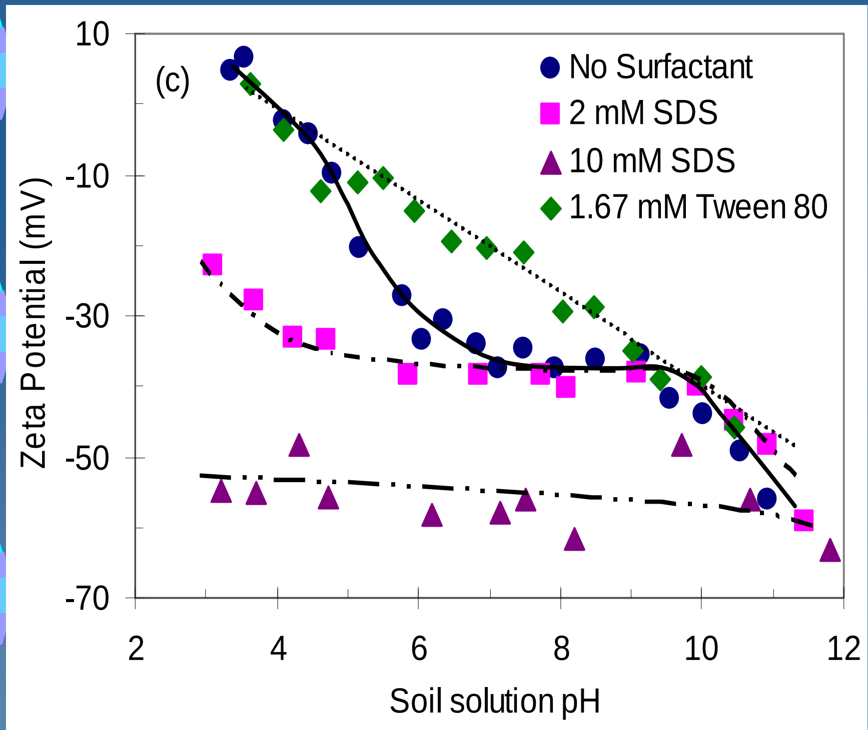
<pH effects>

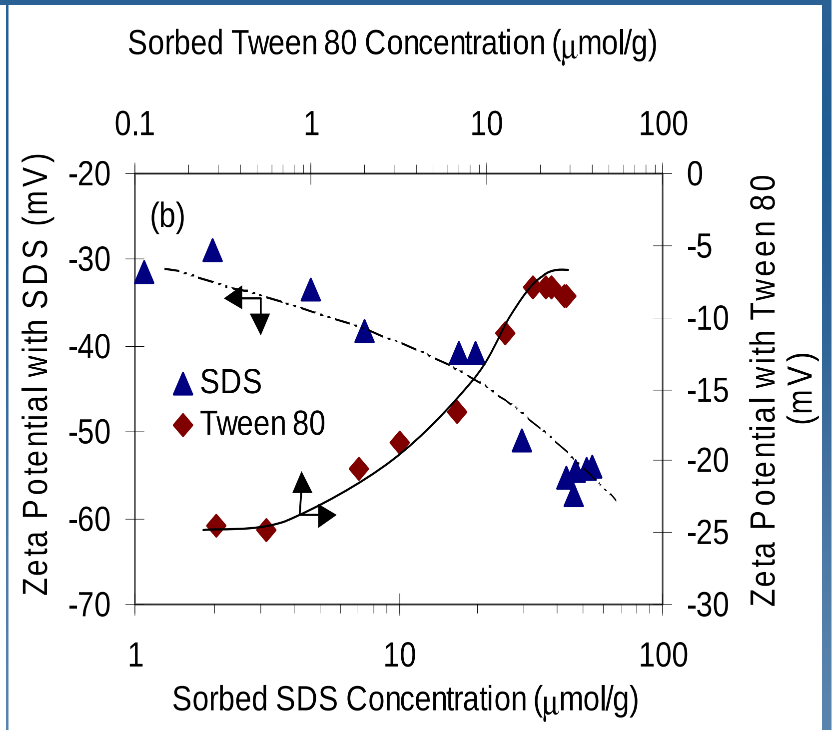


Solution Chemistry Effects on SER

- Zeta potential of kaolinite

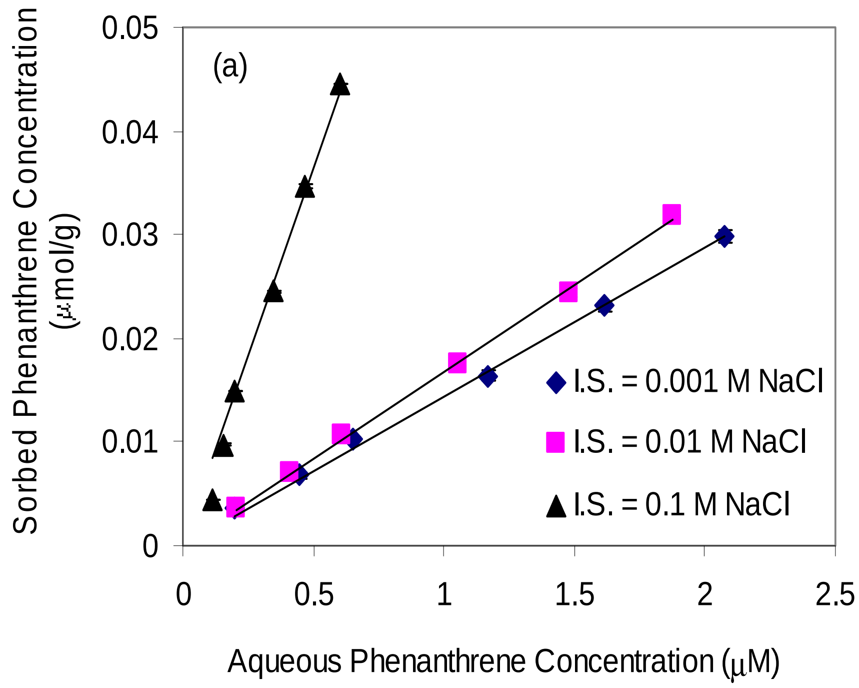
<pH effect> <Effect of sorbed surfactant>

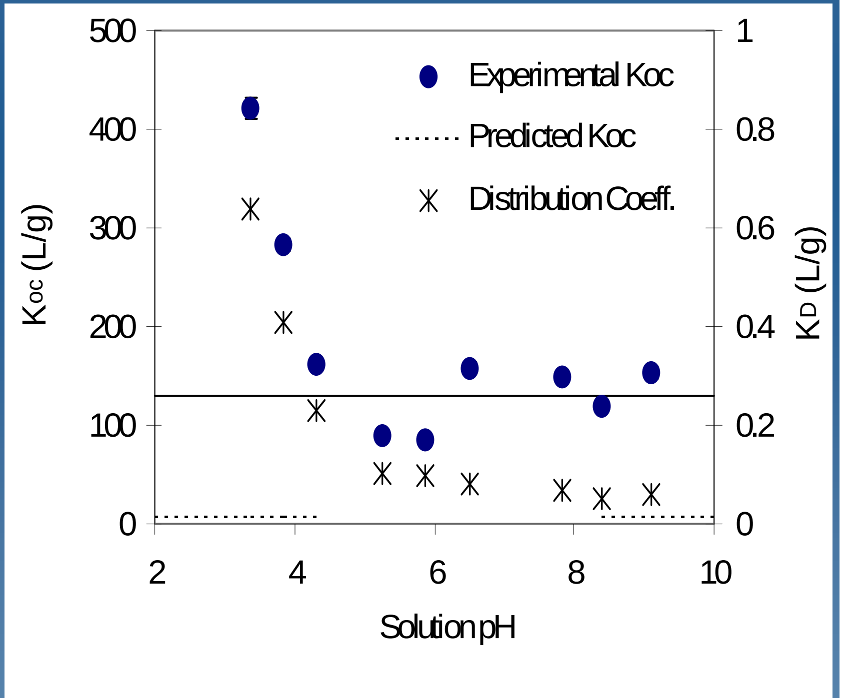




Solution Chemistry Effects on SER

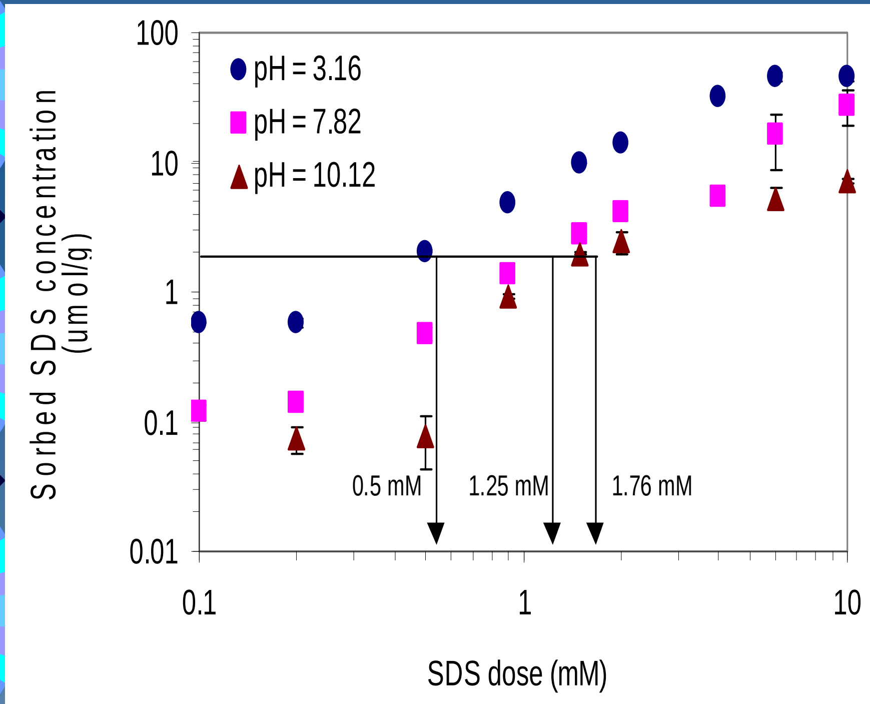
- Phenanthrene partitioning to sorbed SDS (K_{ss})
- <Ionic strength effects> <pH effects>

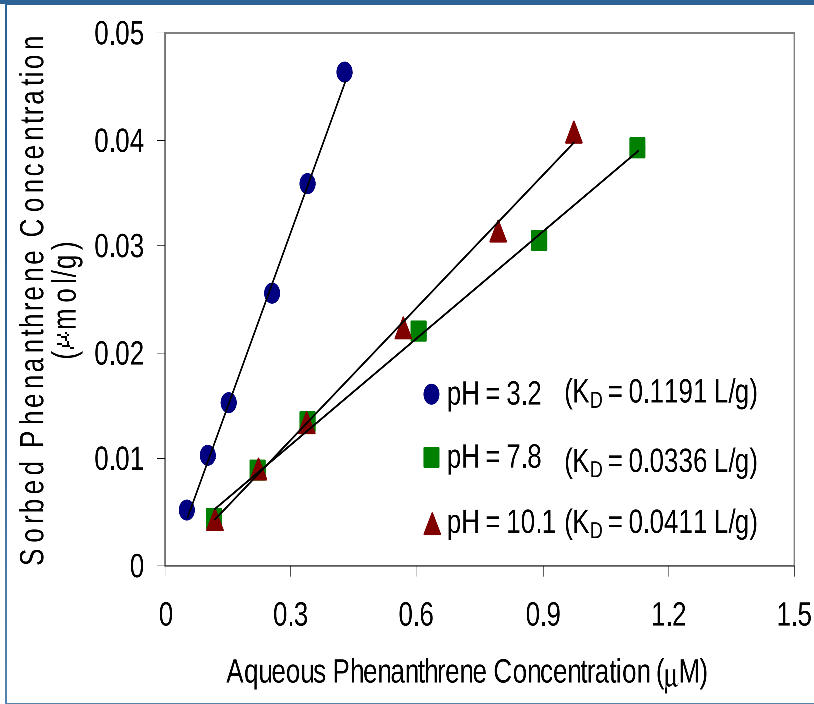




Solution Chemistry Effects on SER

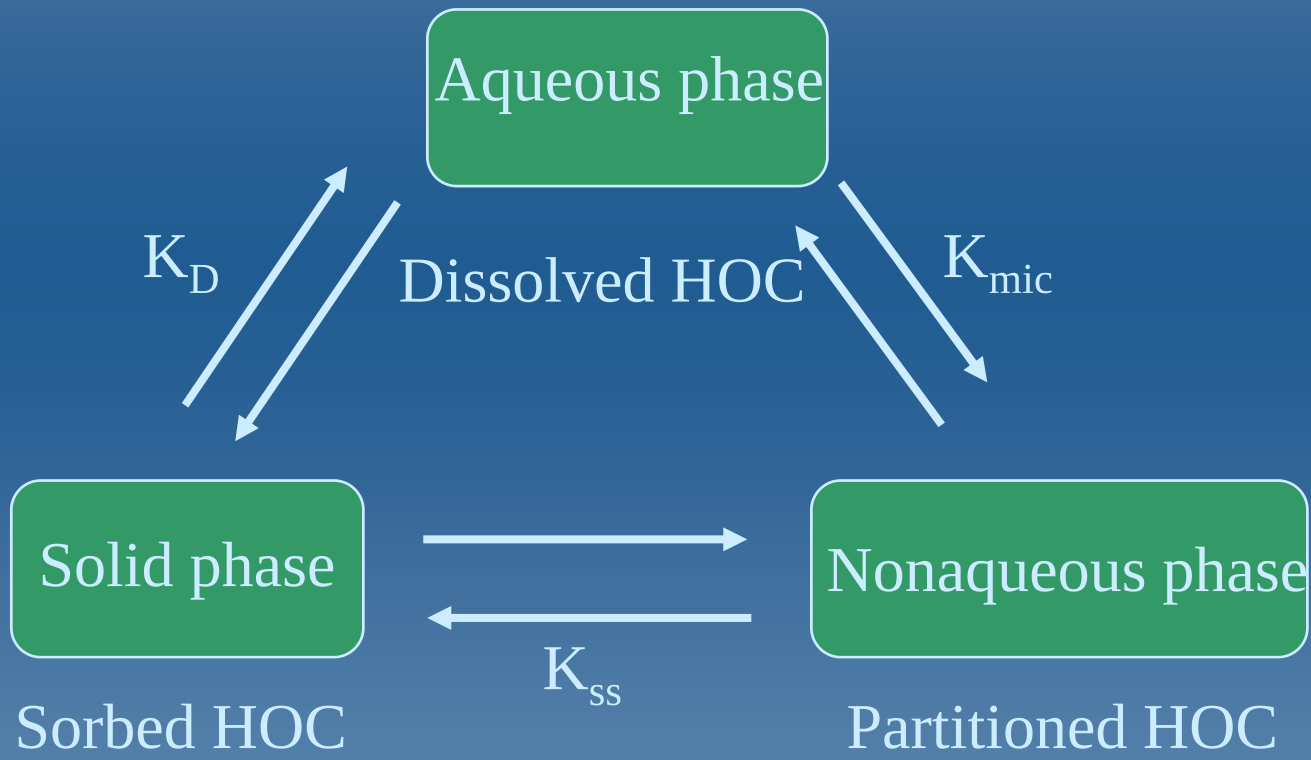
- Effect of pH on structural difference of sorbed surfactant (admicelle)
- Same mass of sorbed SDS on kaolinite - different pH





Numerical simulation of SER

- HOC distribution in multiphase



Numerical simulation of SER

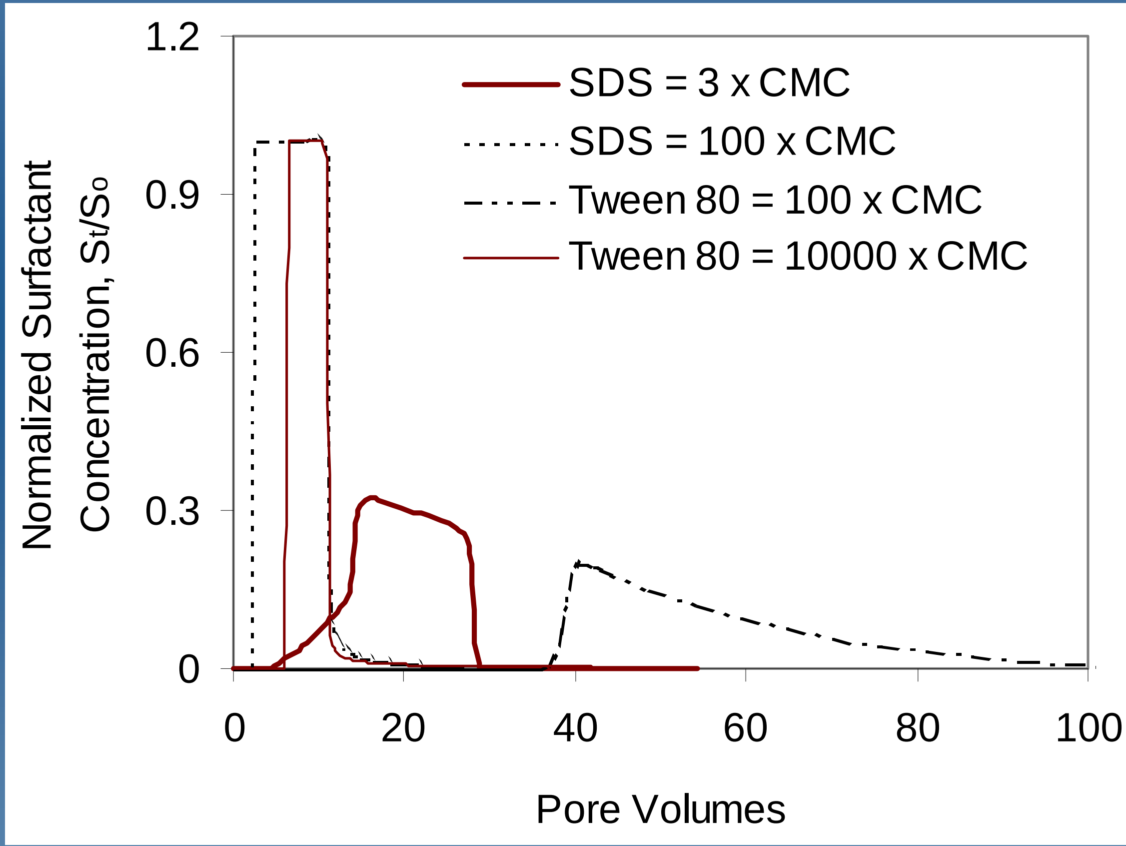
Surfactant → Sandy Aquifer contaminated with HOC (C_o) →

<u>Predict HOC Removal</u>

- Effluent HOC (C_t)
- Surfactant BTC

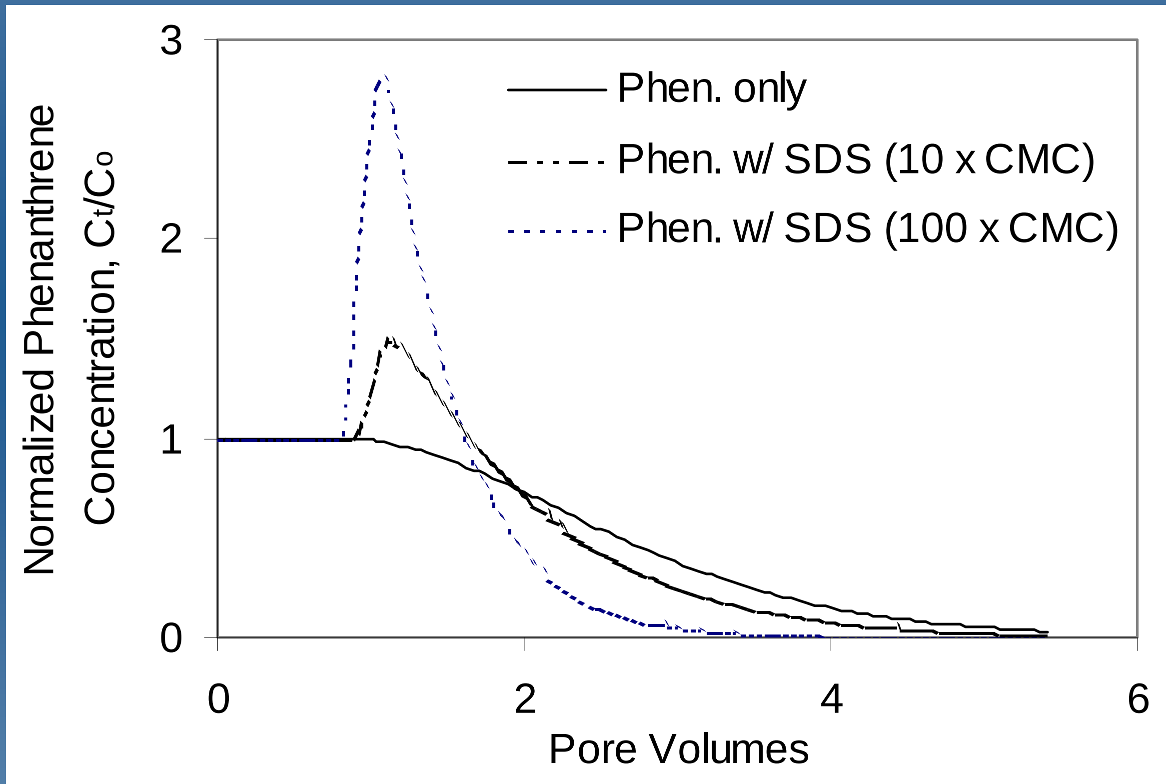
Numerical simulation of SER

- Surfactant breakthrough curve (5 P.V.)



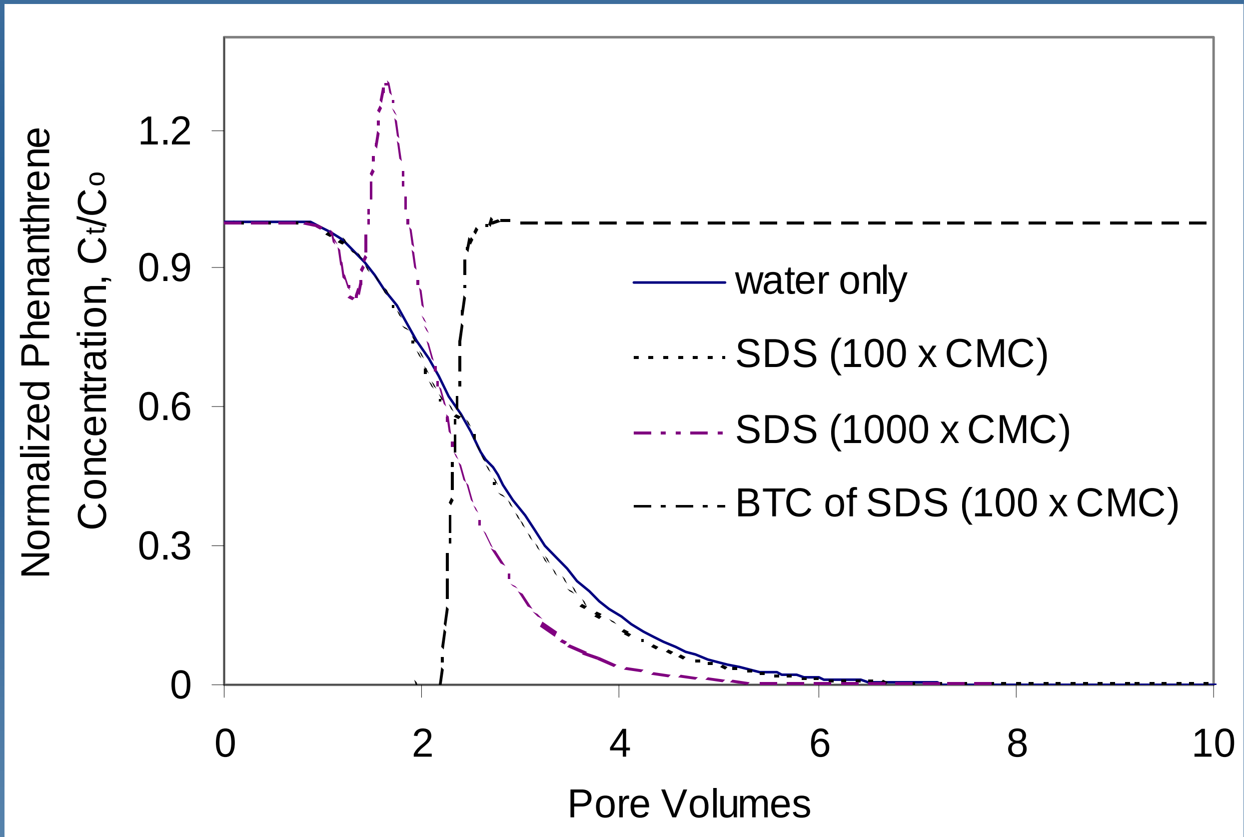
Numerical simulation of SER

- Phenanthrene + SDS (no sorption)



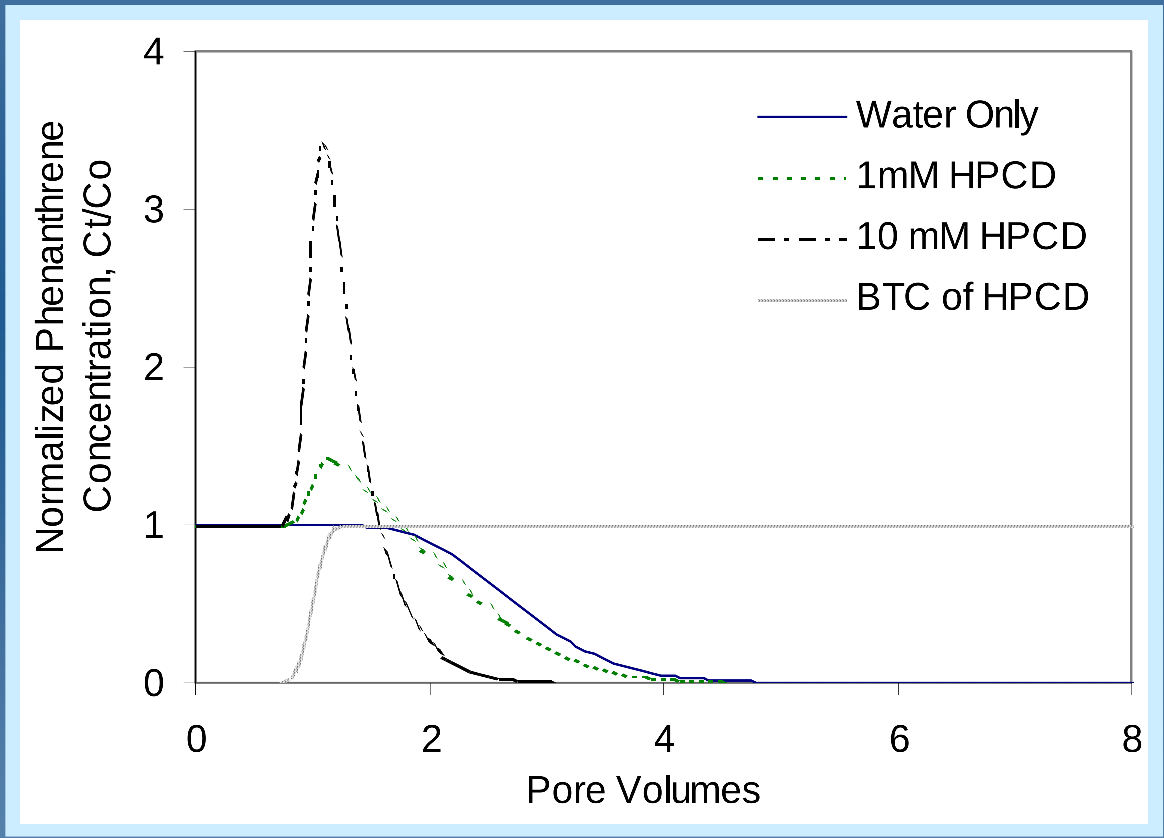
Numerical simulation of SER

- Phenanthrene + SDS (sorption)



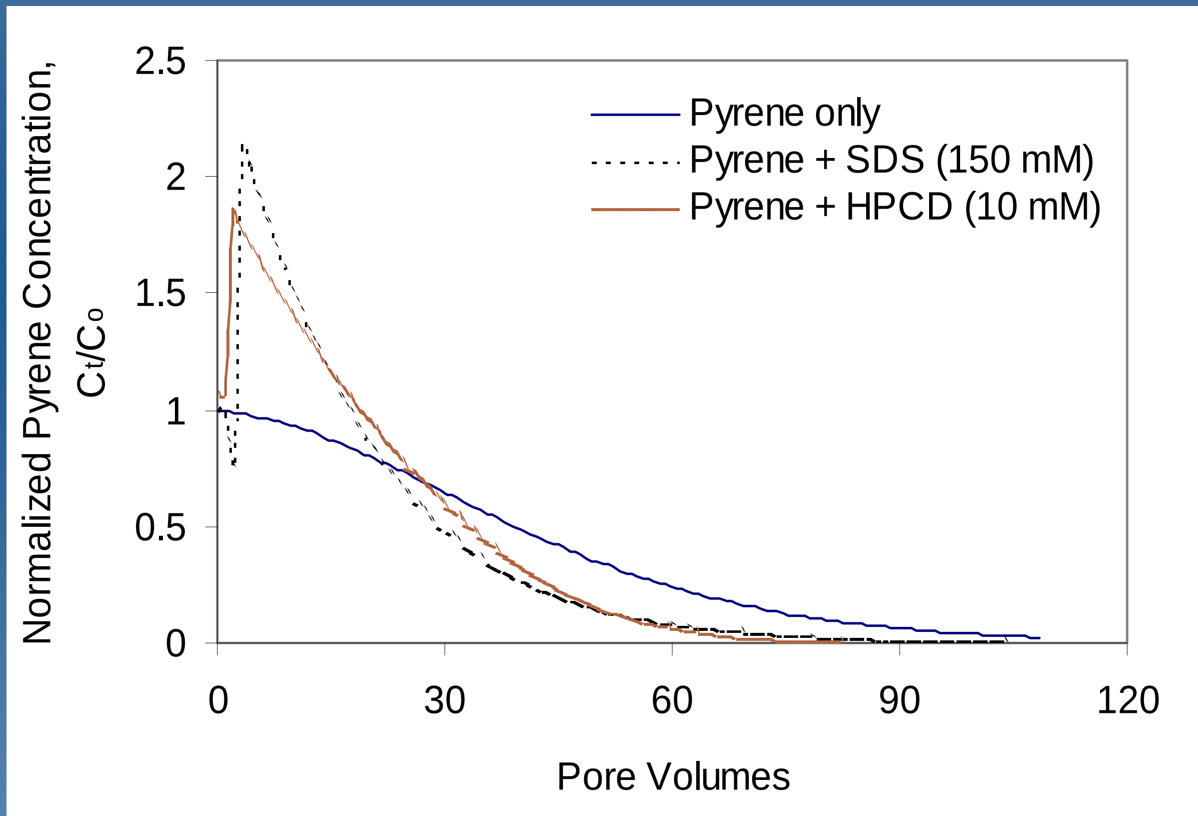
Numerical simulation of SER

- Phenanthrene + HPCD



Numerical simulation of SER

- Pyrene + HPCD or SDS



Role of sorbed surfactant

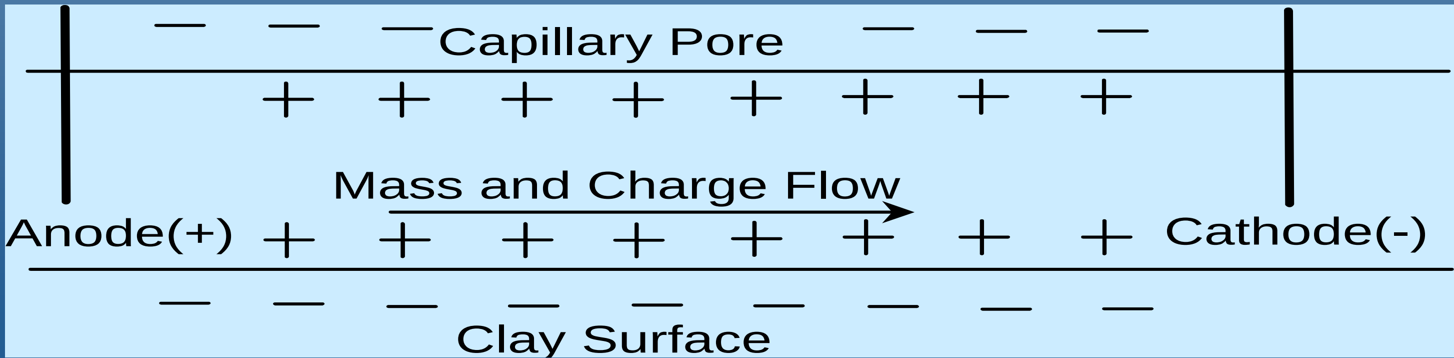
- High affinity of sorbed surfactants for HOCs offers promising alternatives for removing HOCs from water (barrier walls, landfill liners)
- HOC partitioning to sorbed surfactants relative to surfactant micelles reduces the effectiveness of SER
- SER can be effective for HOCs with higher retardation factors than those for the surfactants
- Cyclodextrin is a promising candidate for SER applications because of its low sorption to the solid phase

Surfactant type for EK operation ?

- SDS
  - Higher sorption at low pH
  - $K_{ss} > K_{mic}$ (and higher K_{ss} at low pH)
- Tween 80
  - Higher sorption at low pH
  - $K_{ss} > K_{mic}$
  - Higher zeta potential with sorbed Tween 80
- HPCD
  - No sorption and no change in zeta potential
  - pH-independent HOC solubilization

Electrokinetic Removal of HOC

- Electrokinetic process



- Electroosmotic Flow (EOF)

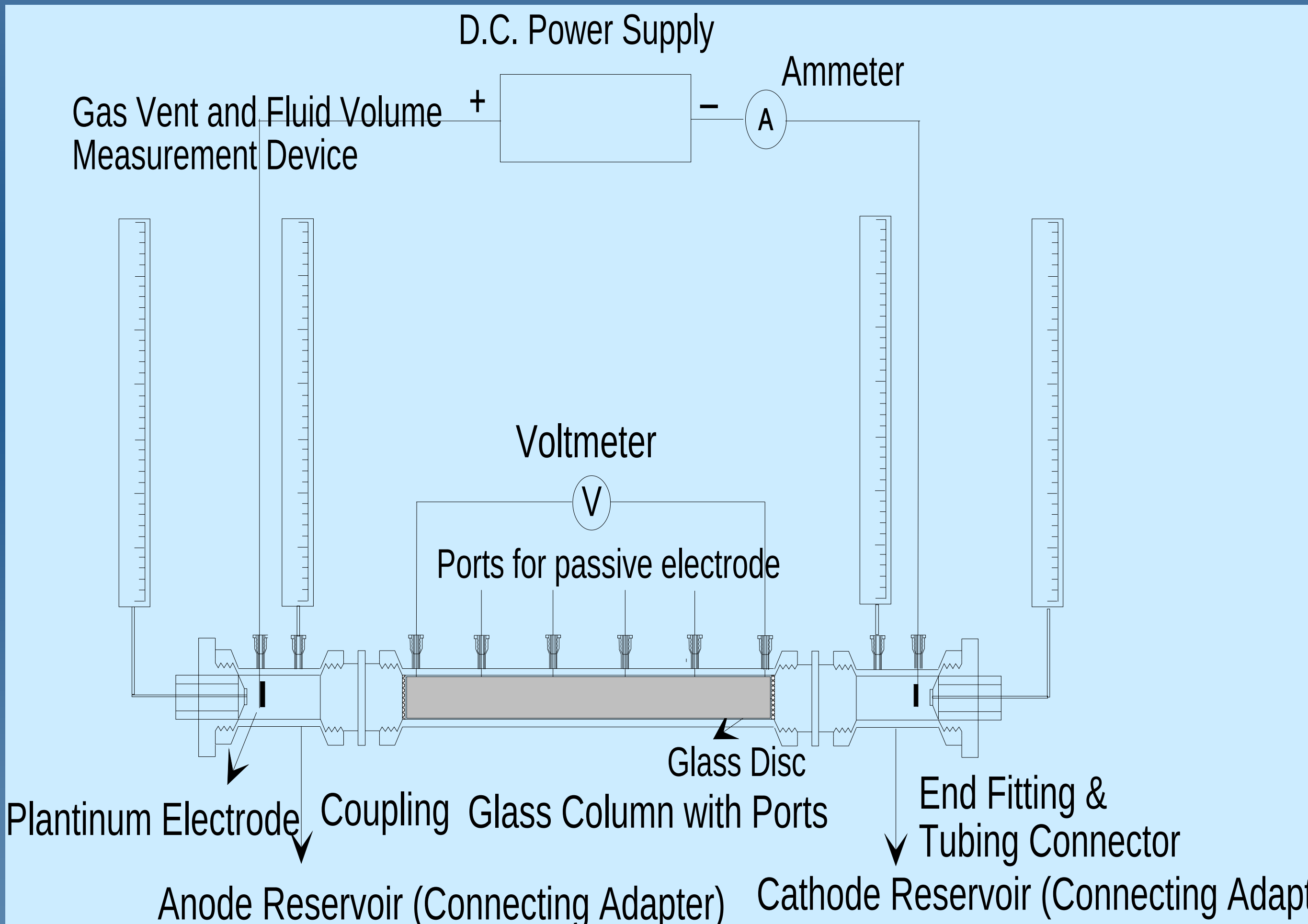
$$u_{EOF} = \frac{\varepsilon \cdot \varsigma \cdot E}{\mu \cdot \tau^2} = k_e \cdot E, \varsigma \text{ is zeta potential}$$

- Electrolysis

$2H_2O - 4e^- \Leftrightarrow 4H^+ + O_2$ (Anode)
$4H_2O + 4e^- \Leftrightarrow 4OH^- + 2H_2$ (Cathode)
$[H^+][OH^-] = K_w$

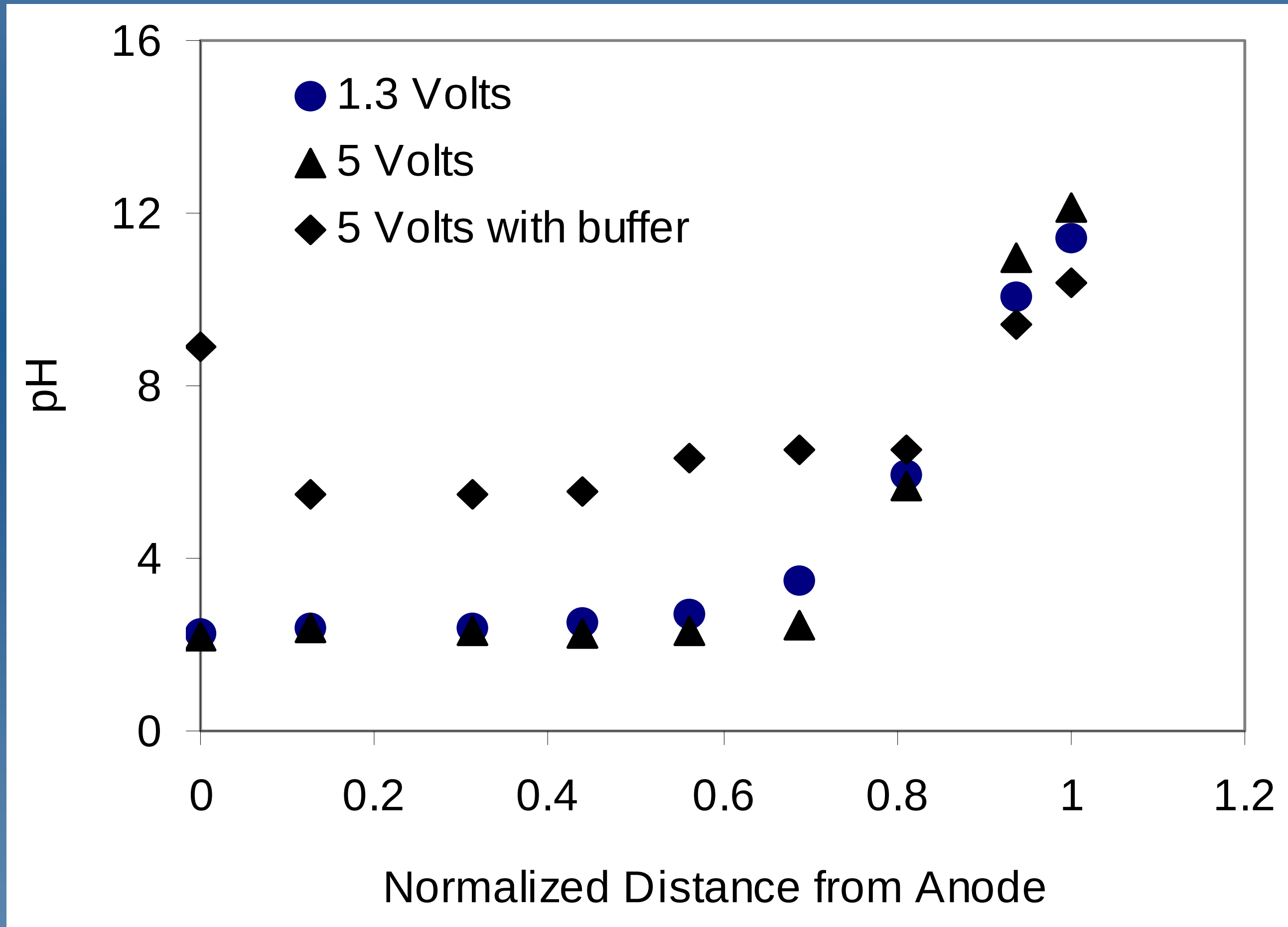
Electrokinetic Removal of HOC

- EK Cell



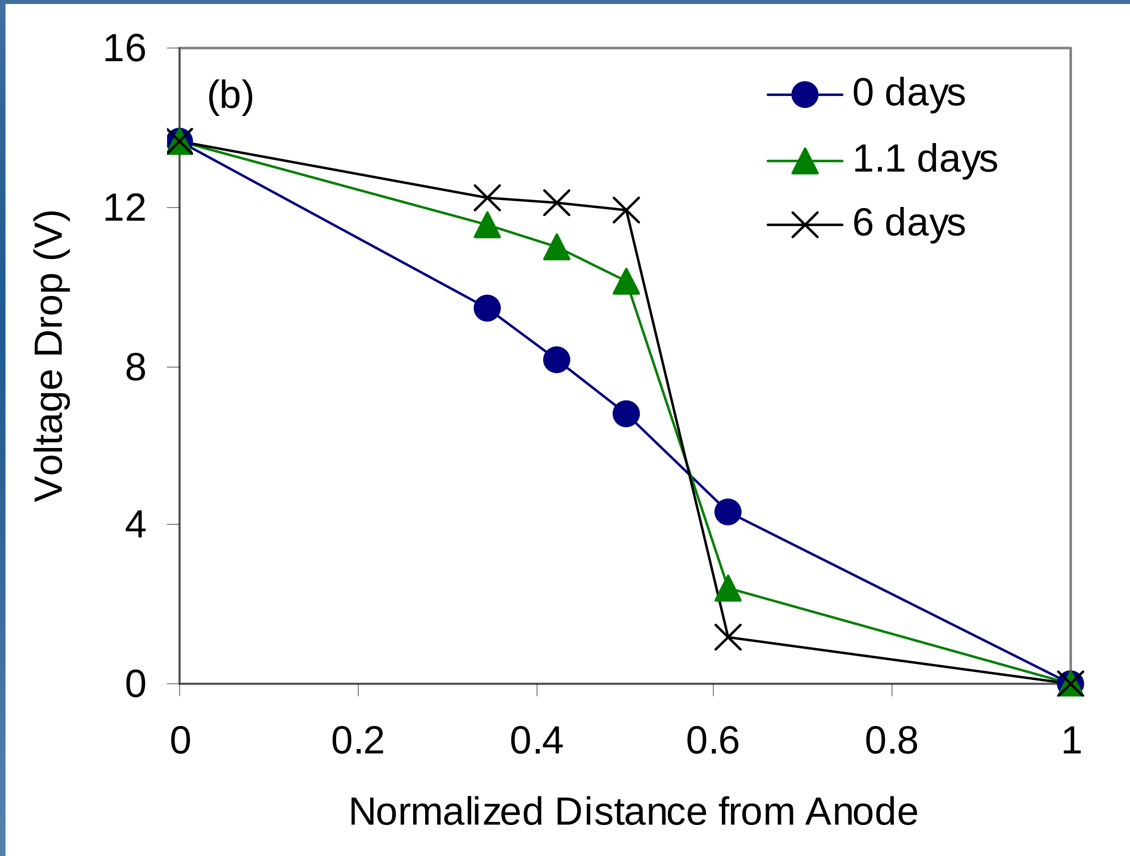
Electrokinetic Removal of HOC

- pH changes



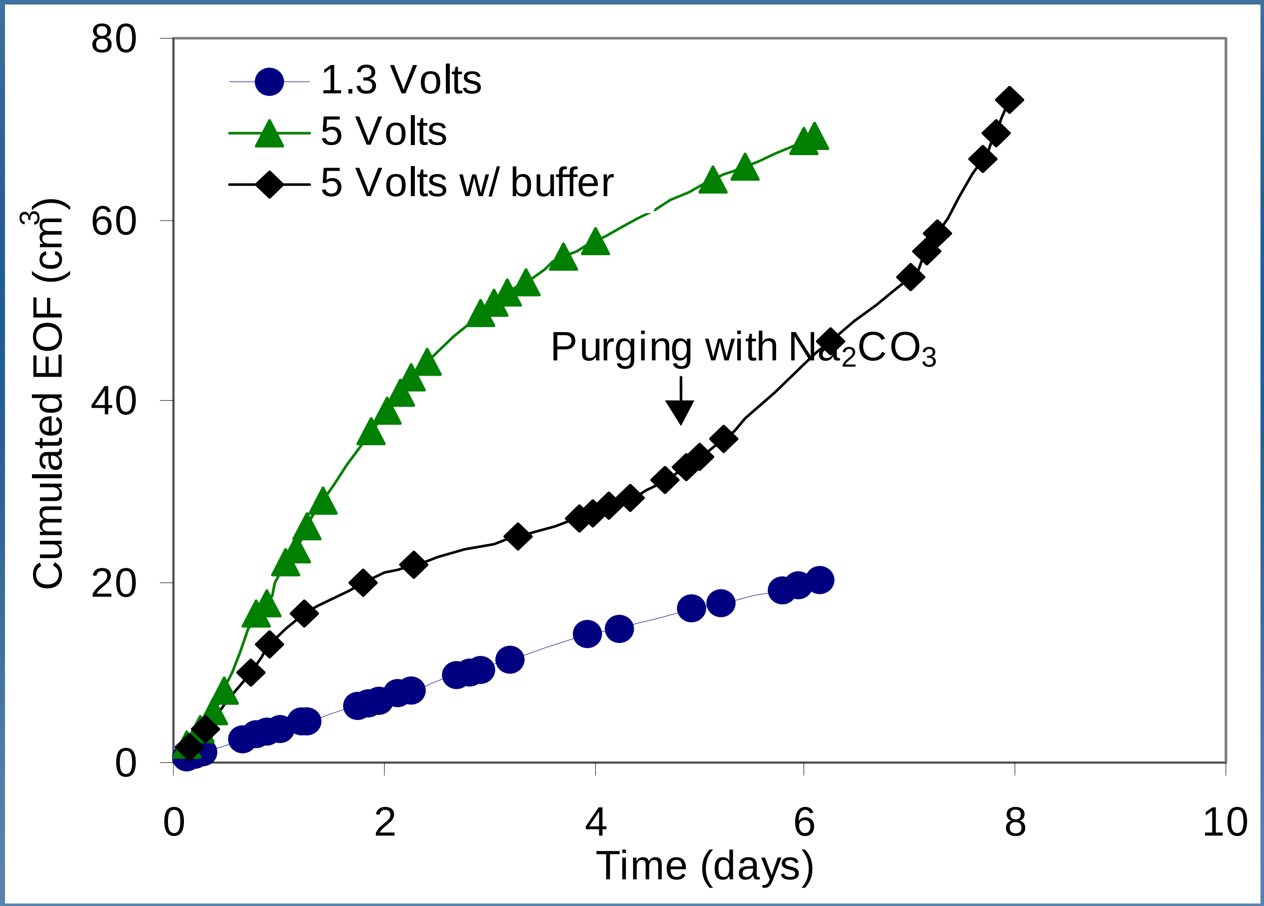
Electrokinetic Removal of HOC

- Voltage changes



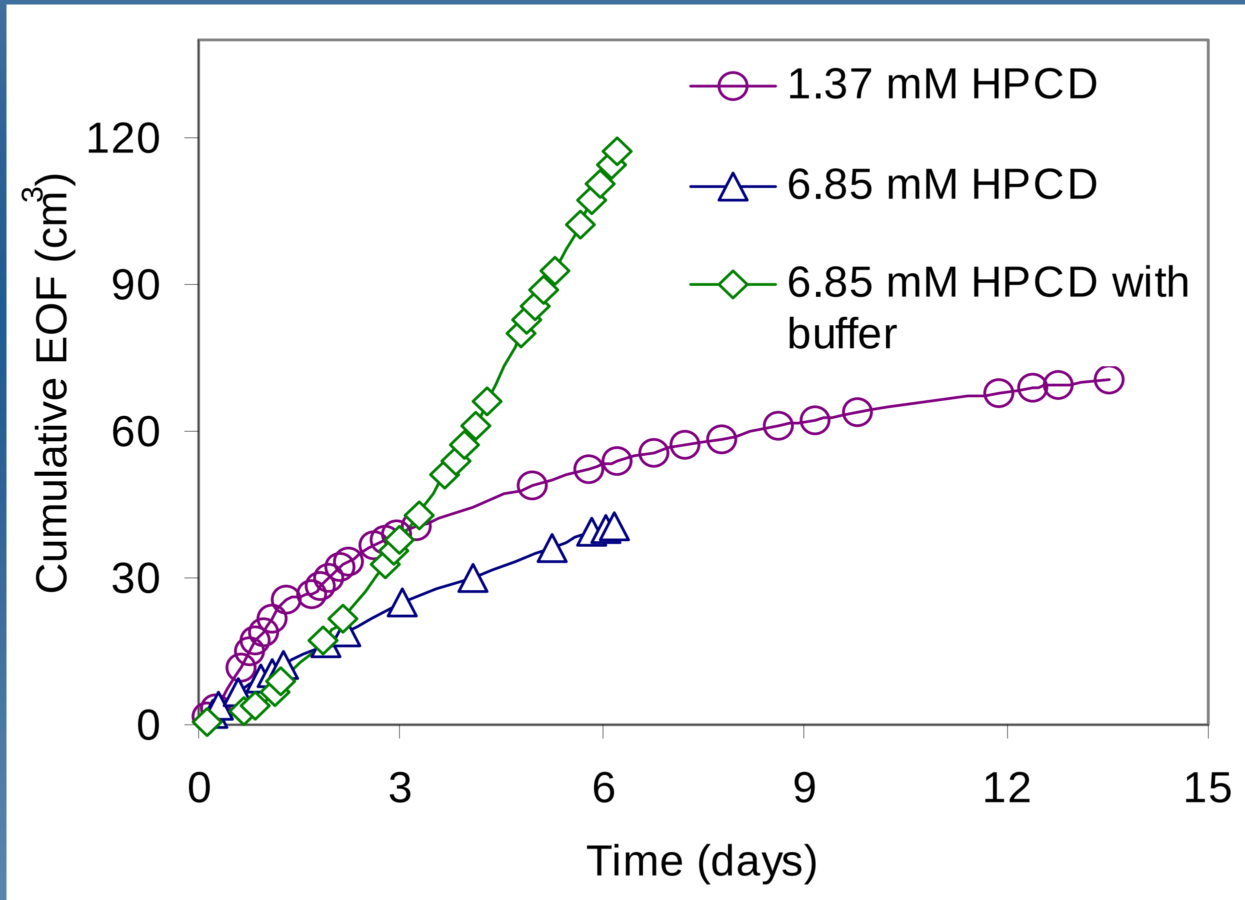
Electrokinetic Removal of HOC

- EOF w/o HPCD



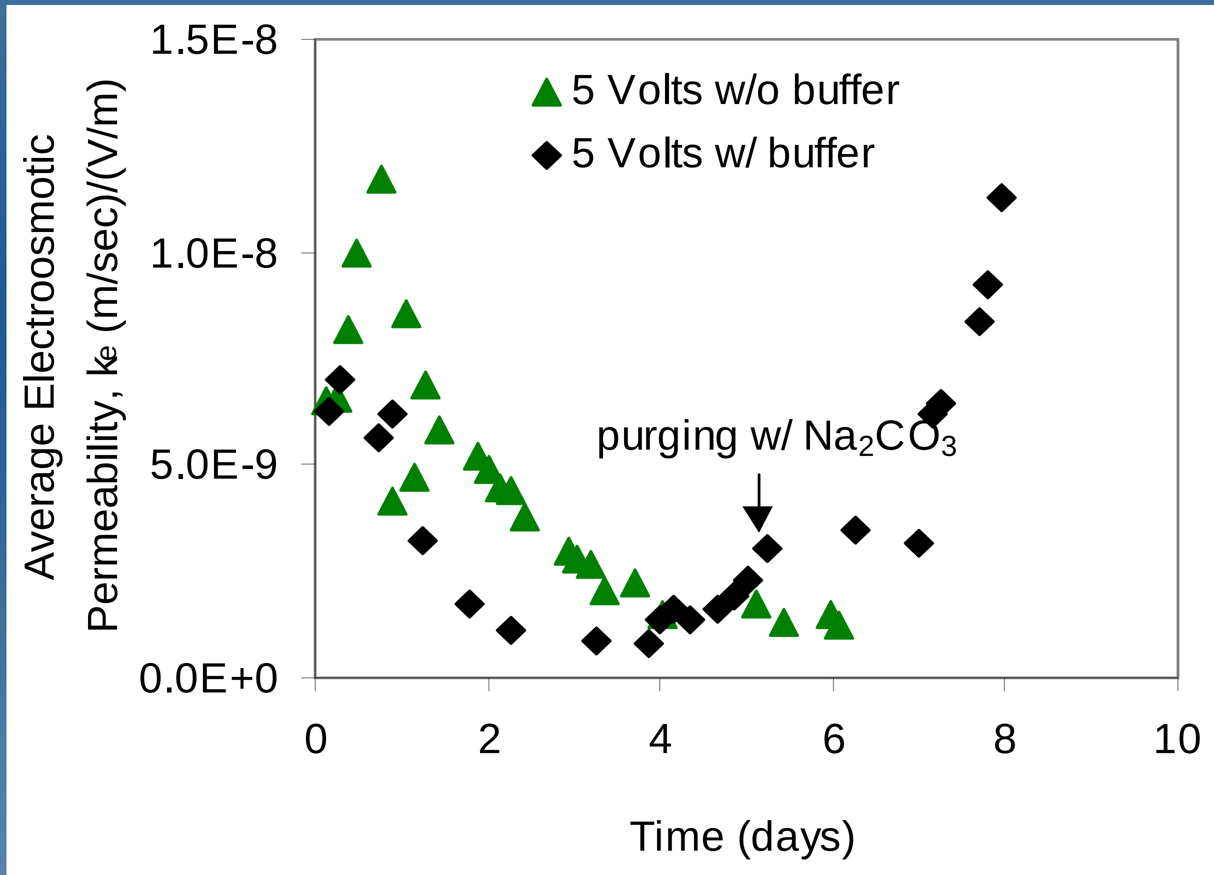
EK Removal of HOC

- EOF w/ HPCD



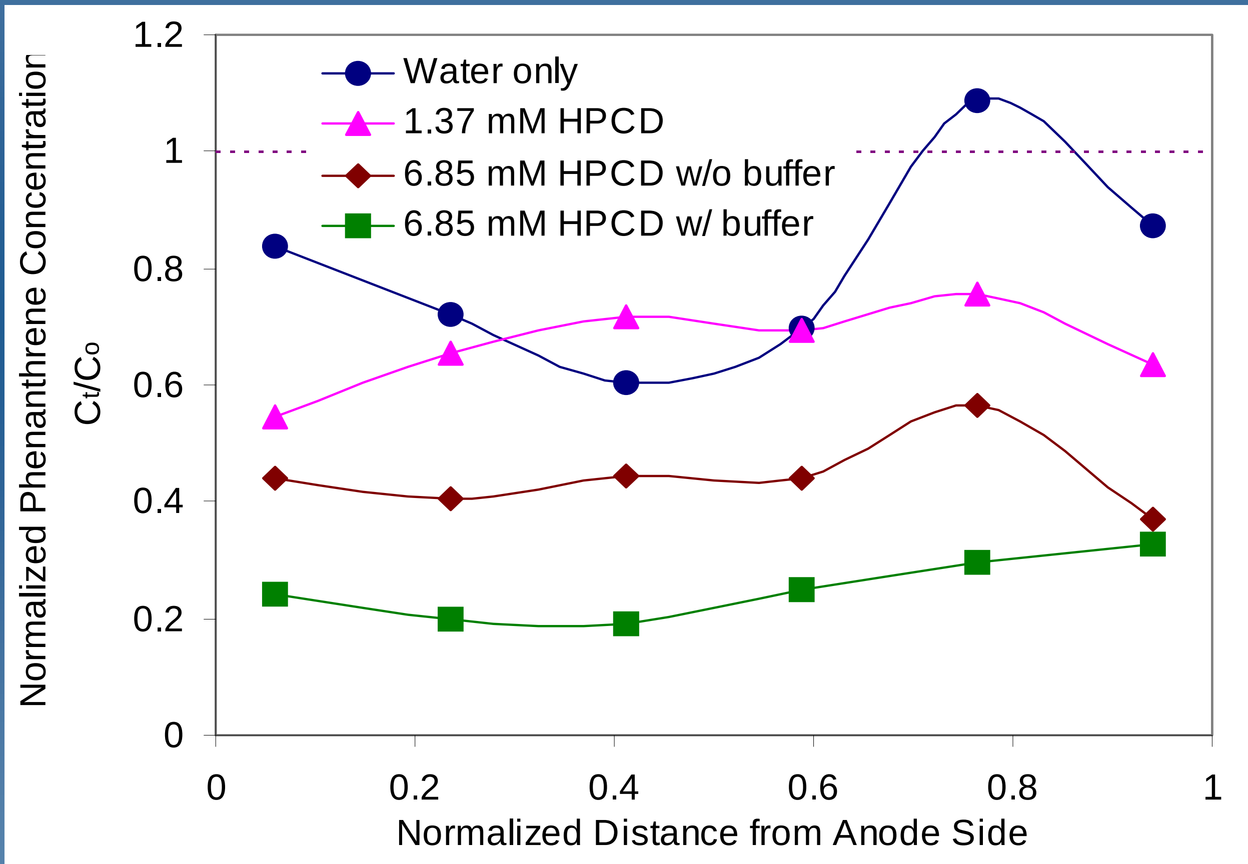
EK Removal of HOC

- Electrokinetic permeability ($k_e = v_{EOF}/E$)



EK Removal of HOC

- Phenanthrene removal



Conclusions

- Surfactant sorption play an adverse role in the removal of HOC from solid phase (increase the HOC retardation)
- HOC partitioning to sorbed surfactant is dependent on the structure of sorbed surfactant
- Electrokinetic combined with HPCD flushing and buffer solution (or keeping the pH high) can effectively remove HOCs in fine soils

Future Research

- Microscopic investigation on the structure of sorbed surfactant as a function of surfactant dose (monolayer/bilayer) and solution pH (bilayer type), and corresponding HOC partitioning capacity
- Use of alternative agents for HOC solubility enhancement (bio-products or DOM)
- Development of numerical model to predict electrokinetic properties of soil with time (EOF, charge flow, pH, and voltage) and corresponding HOC transport

Future Research

- Application of *in-situ* EK process to remove migrated HOC toward cathode region (biodegradation, activated carbon, chemical degradation)

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