Surfactant Selection and Bench-Scale Testing

Center for Petroleum and Geosystems Engineering
The University of Texas at Austin

CPGE

SEAR Workshop

What is SEAR ?

- **SEAR** stands for

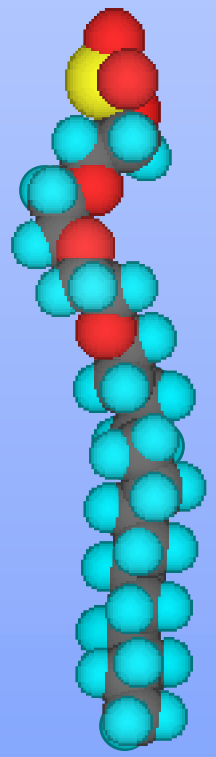
  Surfactant **E**nhanced **A**quifer **R**emediation

- SEAR involves the injection of surfactants to recover NAPL-contaminants by either enhanced solubilization or mobilization due to interfacial tension reduction.

Surfactant Ionic Type Classification

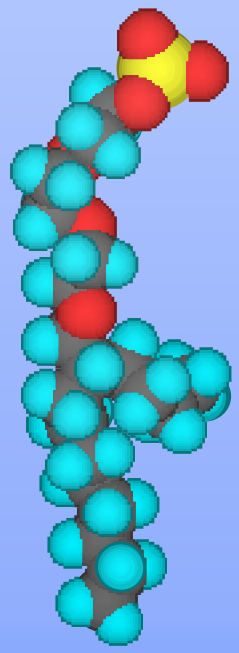
- Surfactants
  - Anionics
    - Soaps
    - Sulfates
    - Sulfonates
    - Phosphates
    - Sulfosuccinates
  - Nonionics
    - Ethoxylated alcohol
    - Ethoxylated sorbitan fatty ester
    - Sulfoxides
  - Cationics
    - Amine oxides
    - Amine salts
    - Quaternary ammonium
  - Amphoterics
    - Imidazoline
    - Betaines
    - Sulfobetaines
    - Amino acid
    - Lecithins

Types of Alcohol Ether Sulfate Surfactants



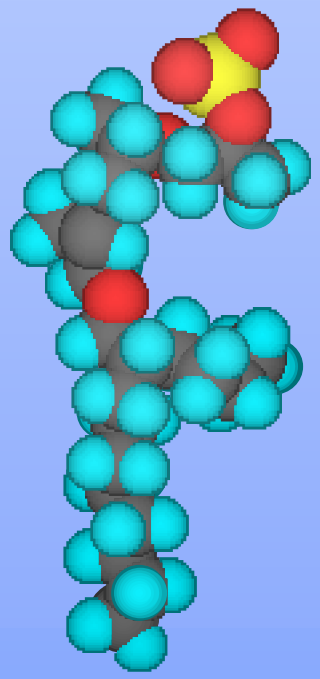
C14 EO3-sulfate

(linear alcohol)



C14 EO3-sulfate

(C4 branch at the #2 carbon)

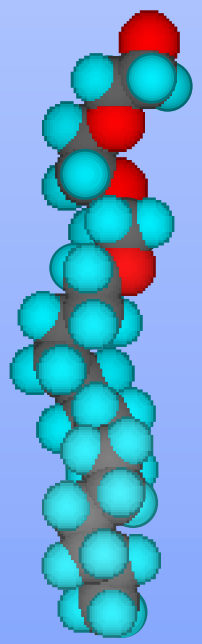


C14 PO3-sulfate

(C4 branch at the #2 carbon; propylene oxide instead of ethylene oxide)

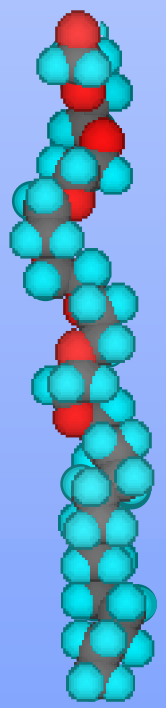
Examples of Nonionic Structures

Alcohol Ethoxylates



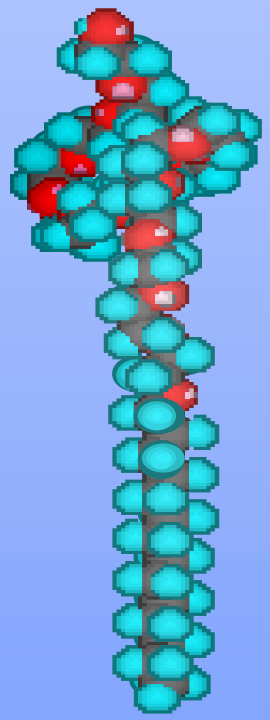
C14 EO3

HLB = 7.7



C14 EO7

HLB = 11.9



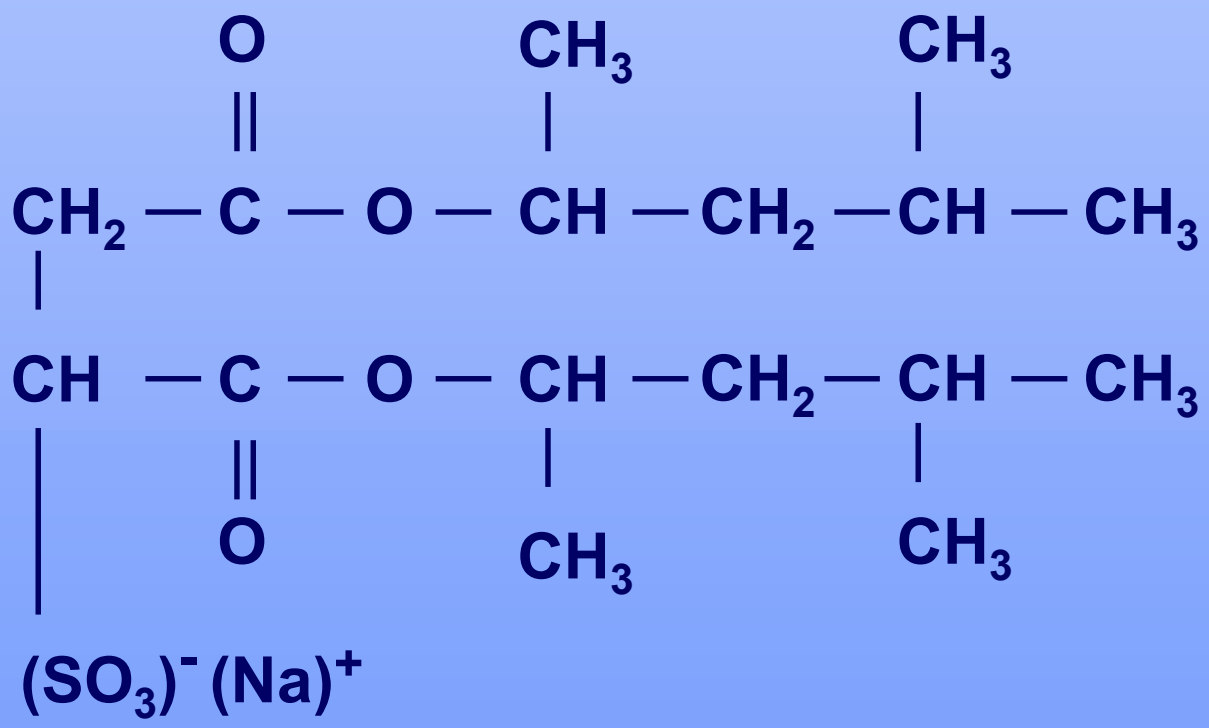
C14 EO14

HLB = 14.9

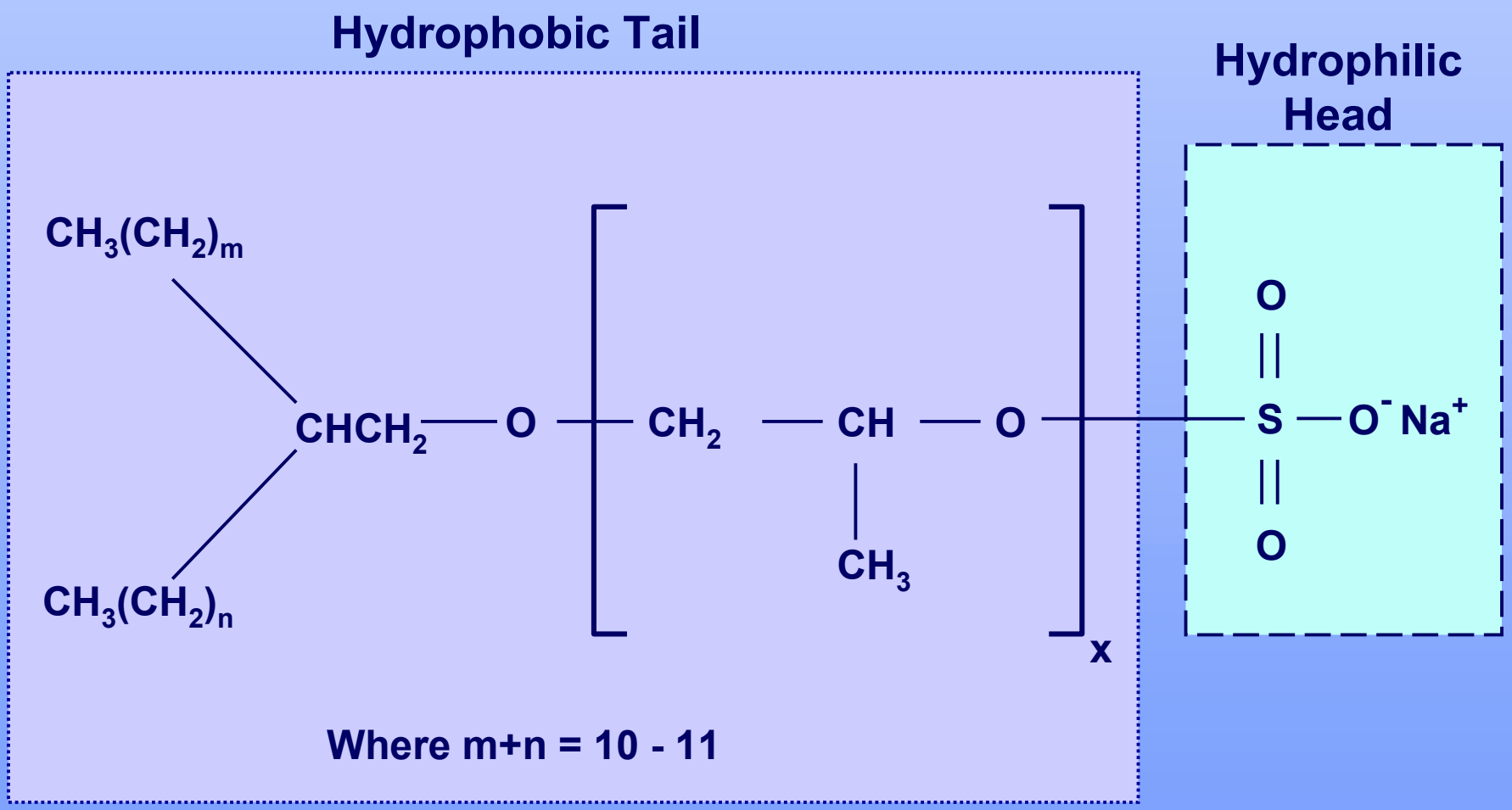
Sodium Dihexyl Sulfosuccinate

(Di-1,3-Dimethyl Butyl Sulfosuccinate, Sodium Salt)
Trade Name: Aerosol MA

Surfactants are surface active agents. They are molecules composed of two differing parts: a lyophobic tail and a lyophilic head. This structure leads to the molecule's interesting behavior.

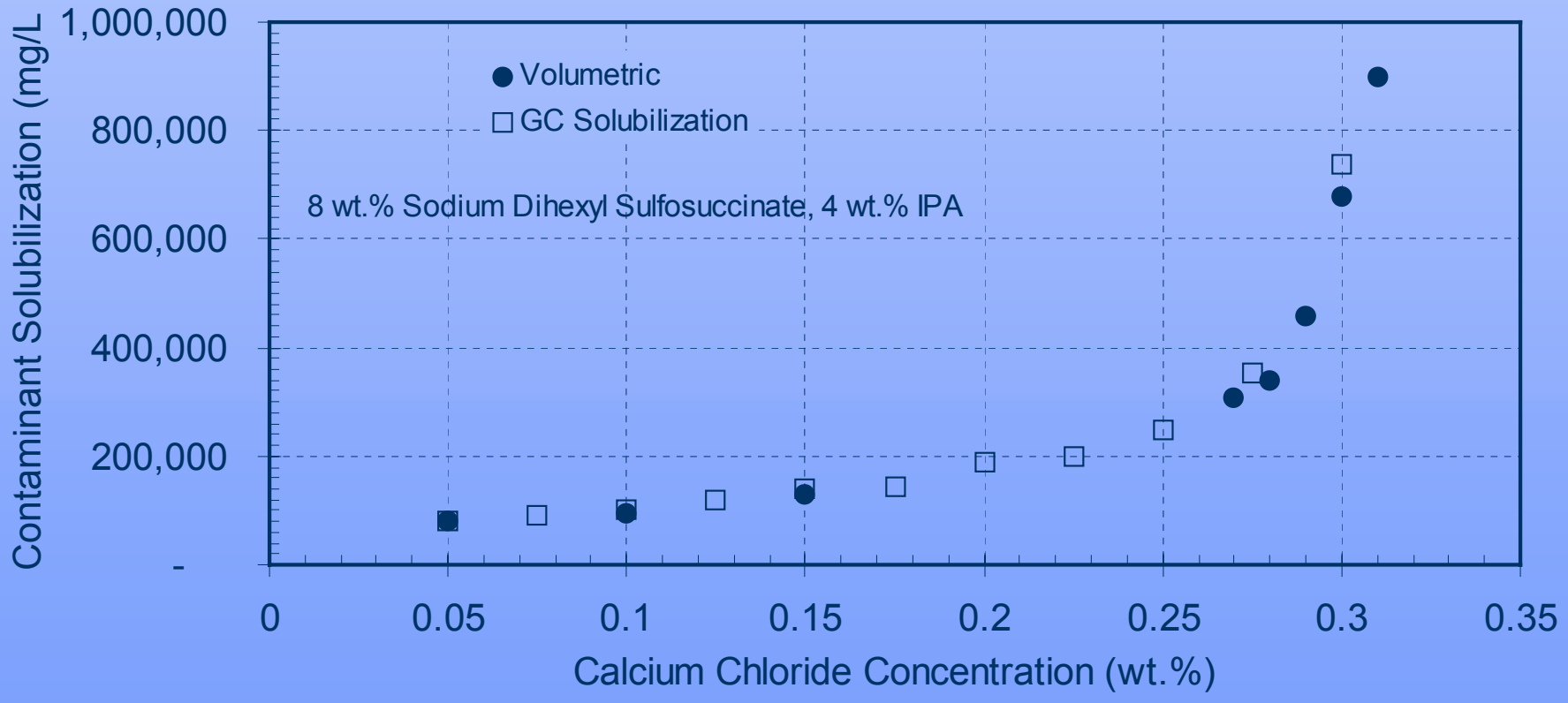


Custom Designed Surfactant



How Surfactants Work: Solubilization

- **Surfactants can enhance contaminant solubilization**

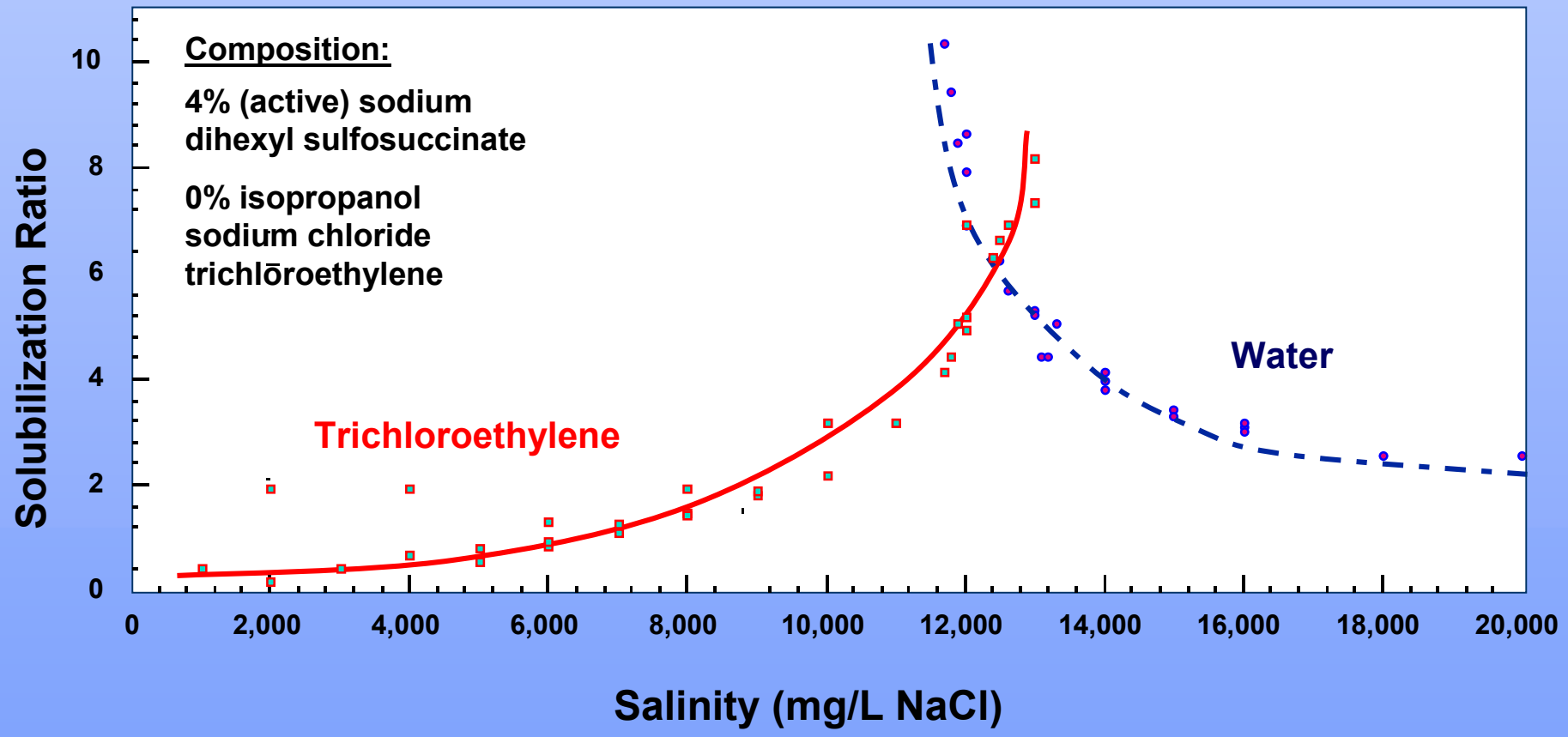


How Surfactants Work: Mobilization

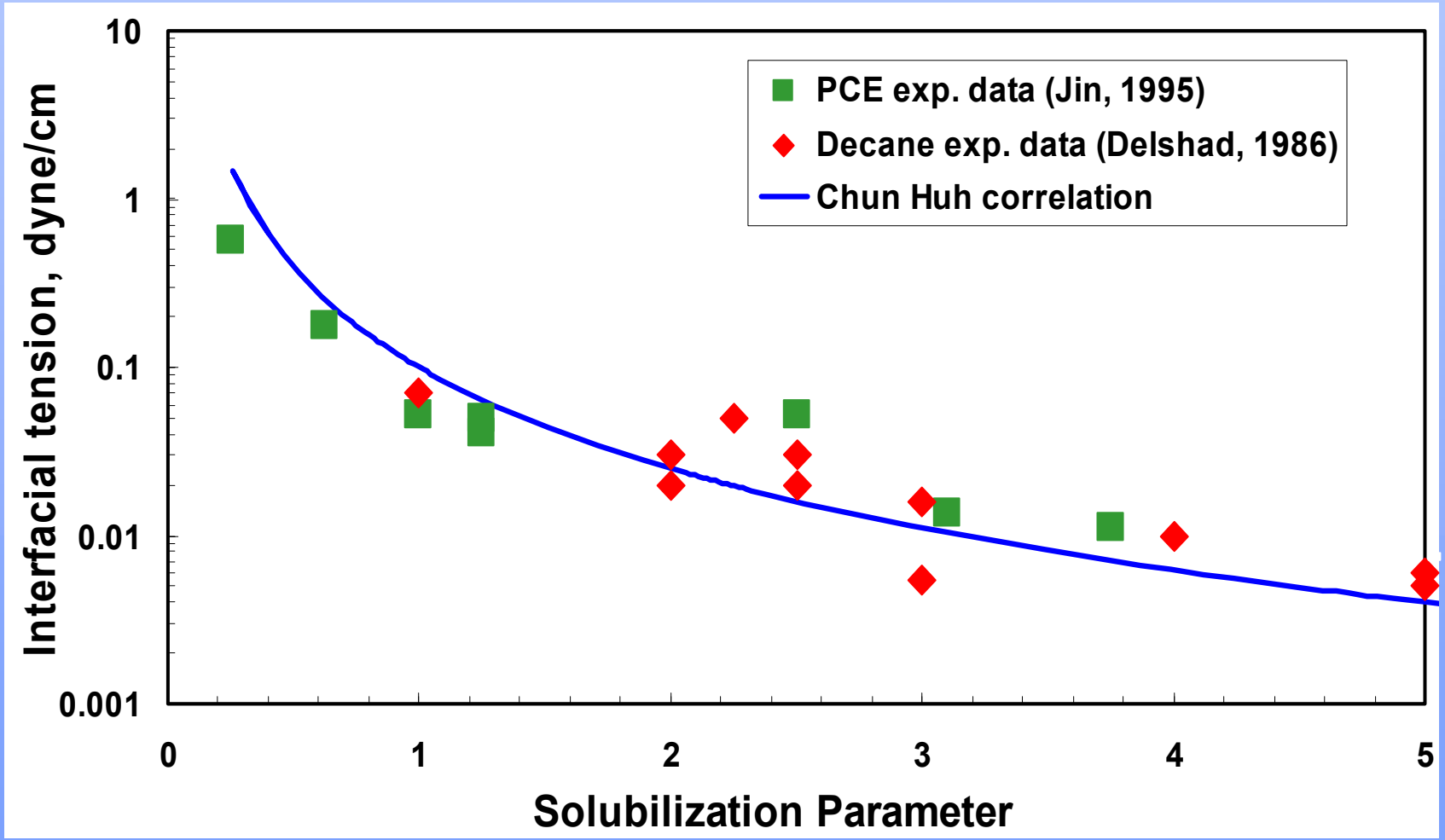
- Surfactants reduce interfacial tensions thereby allowing NAPL to be recovered by mobilization

	Interfacial Tension at 23°C, dynes/cm
Hill AFB DNAPL-water	~ 9
MCB Camp Lejeune DNAPL-water	~ 10
4% MA, 8% IPA, 9,350 mg/L NaCl, TCE	0.02
8% MA in Hill AFB Source Water, Hill AFB DNAPL	0.2
4% MA, 4% IPA, 11.250 mg/L NaCl, Hill AFB DNAPL	0.01
4% MA, 25,000 mg/L NaCl, PCE	0.14

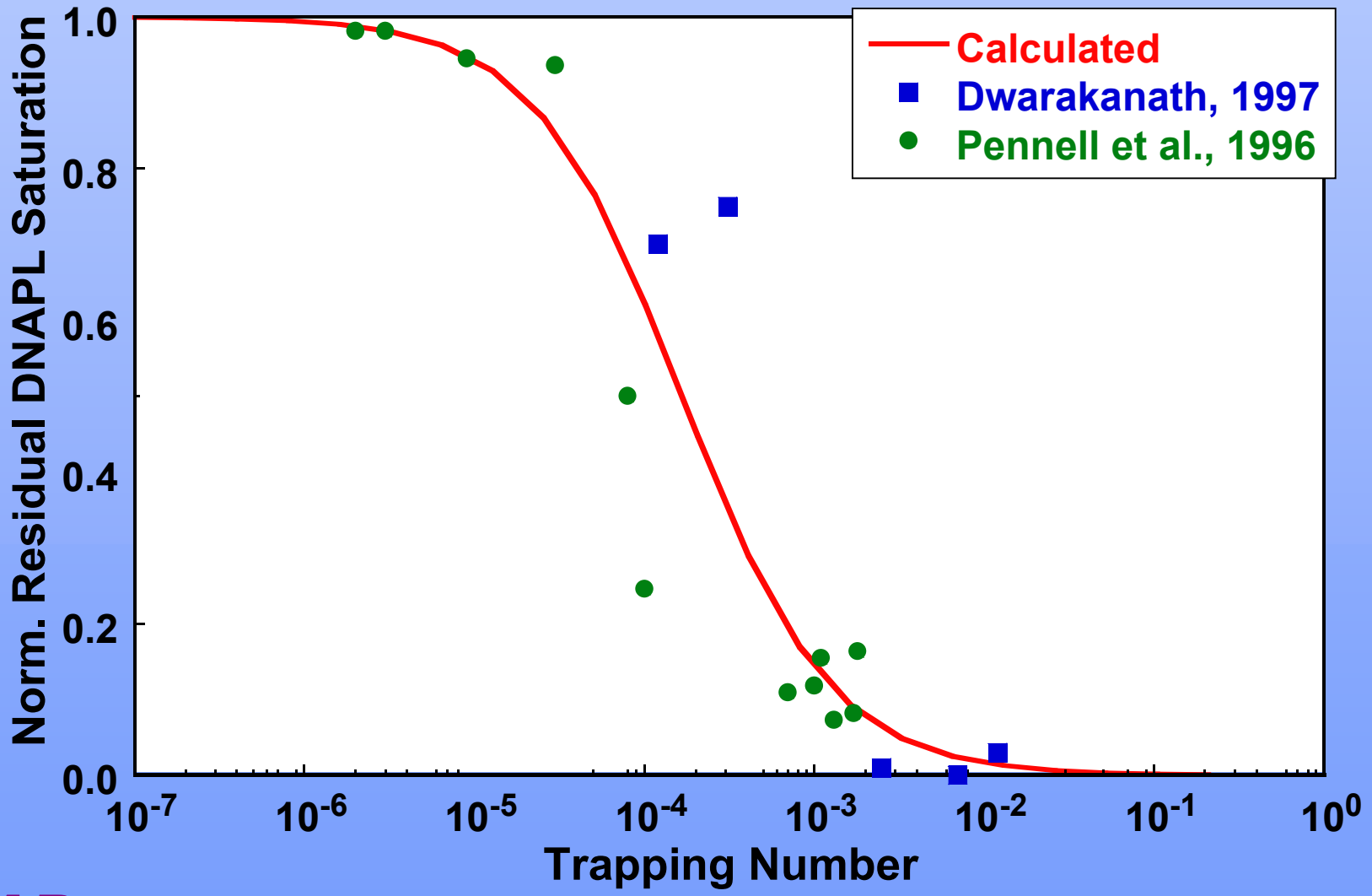
Salinity Scan



Comparison of Chun Huh Predicted and Measured Interfacial Tensions



DNAPL Mobilization



Critical SEAR Remediation Variables

- Microemulsion phase behavior
- Interfacial tension
- Surfactant adsorption
- Viscosities
- Densities
- Mass transfer and diffusion
- Surfactant biodegradation
- Polymer compatibility and properties
- Cost and availability of chemicals

Surfactant Selection Criteria

- Phase behavior
- Solubilization potential
- Environmental acceptability
- Viscosity of surfactant solutions
- Coalescence behavior
- Transport characteristics in permeable media
- Sorption characteristics

Myths and Misconceptions

- Mass transfer effects limit contaminant solubilization by surfactant
- Surfactants reduce aquifer permeability
- Performance affected by surfactant sorption
- Cannot reduce saturation to less than 2–3%
- Lowering IFT will induce downward DNAPL mobilization
- Can avoid mass transfer limitations by adding cosolvent

Myths and Misconceptions (cont.)

- Can avoid reduction in aquifer permeability by using surfactants that do not form gels/emulsions and liquid crystals
- Can minimize surfactant sorption by using anionic surfactants
- Achieved 0.035% during the 1996 AFCEE demonstration
- Achieved 0.03% during the 1996 AATDF demonstration
- Can use neutral buoyancy SEAR to minimize downward mobilization

Review of Surfactant Behavior

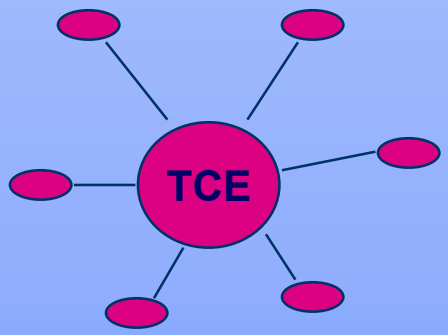
Description of Microemulsions

- Thermodynamically stable and swollen micellar solutions should not be confused with macroemulsions
- Forming stable microemulsions rapidly is cornerstone of application of surfactants for NAPL recovery

Surfactant Phase Behavior

Winsor Type I Behavior

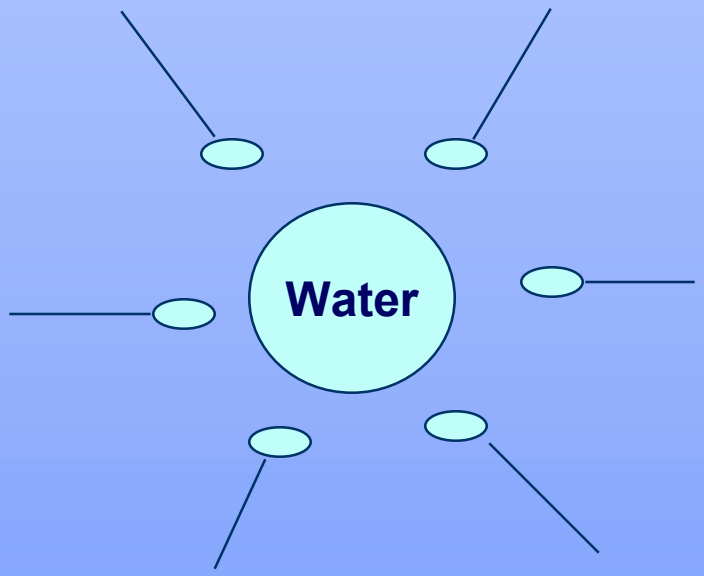
- Oil-in-water microemulsion
- Can solubilize significant volume of contaminant
- Usually associated with solubilization type remediation regimes



Surfactant Phase Behavior (cont.)

Winsor Type II Behavior

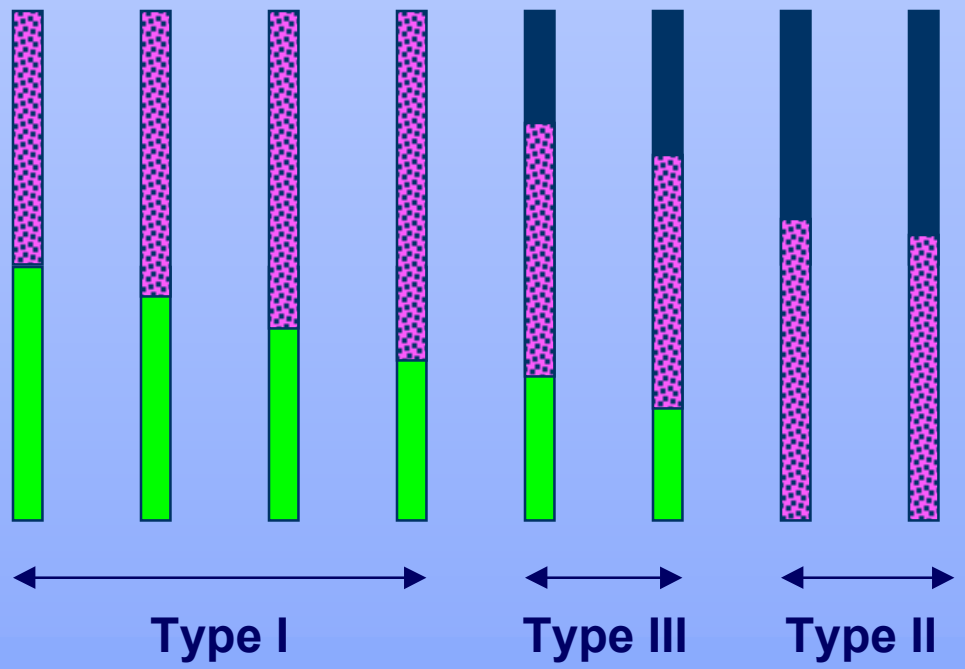
- Water-in-oil microemulsion
- Surfactant lost to the NAPL
- Should be avoided in EOR and SEAR operations



Phase Behavior Experiments

- Phase behavior experiments
  - Measure contaminant solubilization
  - Measure coalescence/equilibration time
  - Determine microemulsion viscosities
- Specific surfactants can be tailored for specific NAPLs, such as in MCB Camp Lejeune and Naval Station Pearl Harbor

Surfactant Phase Behavior (cont.)



Aqueous Phase

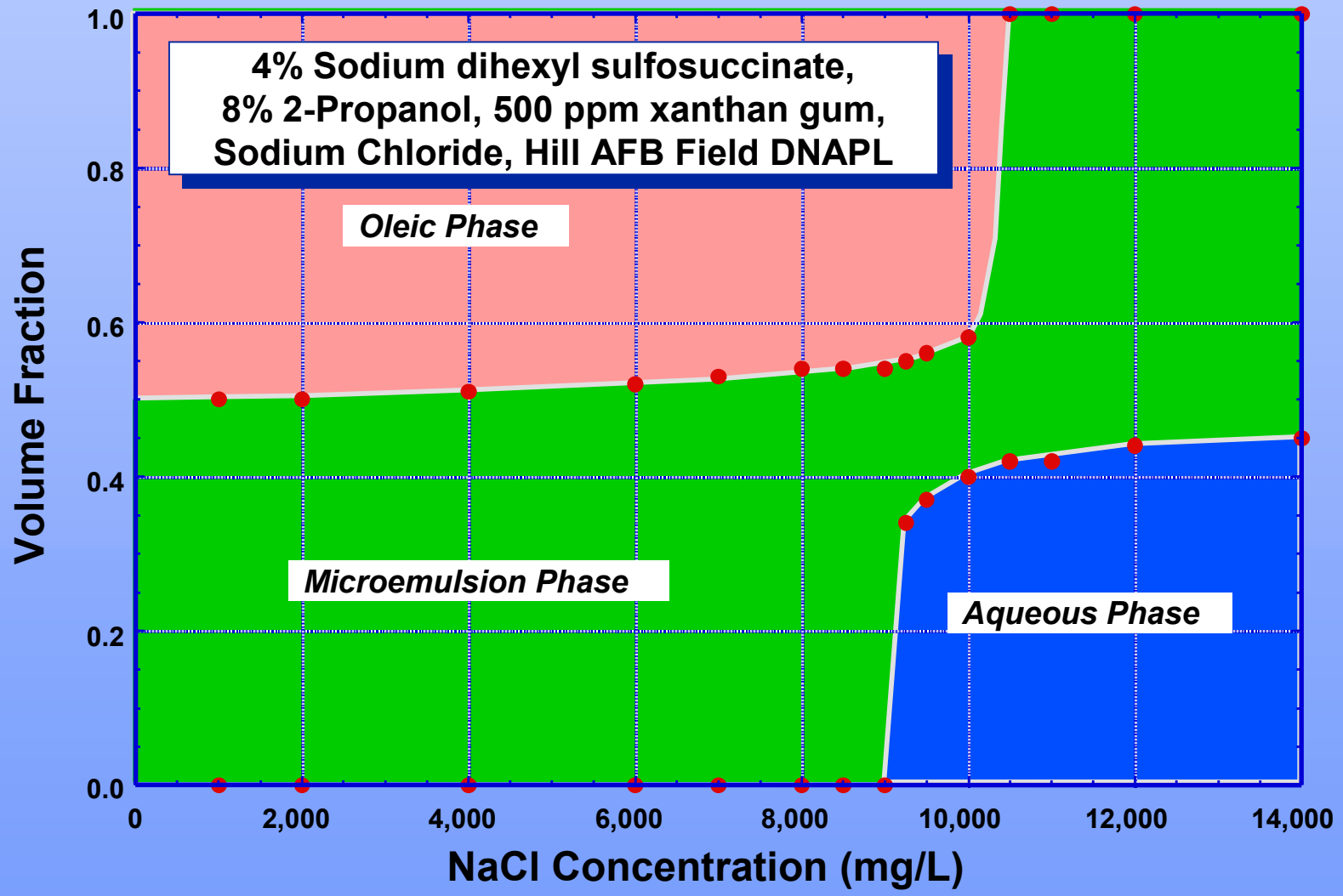
Nonaqueous Phase

Microemulsion Phase

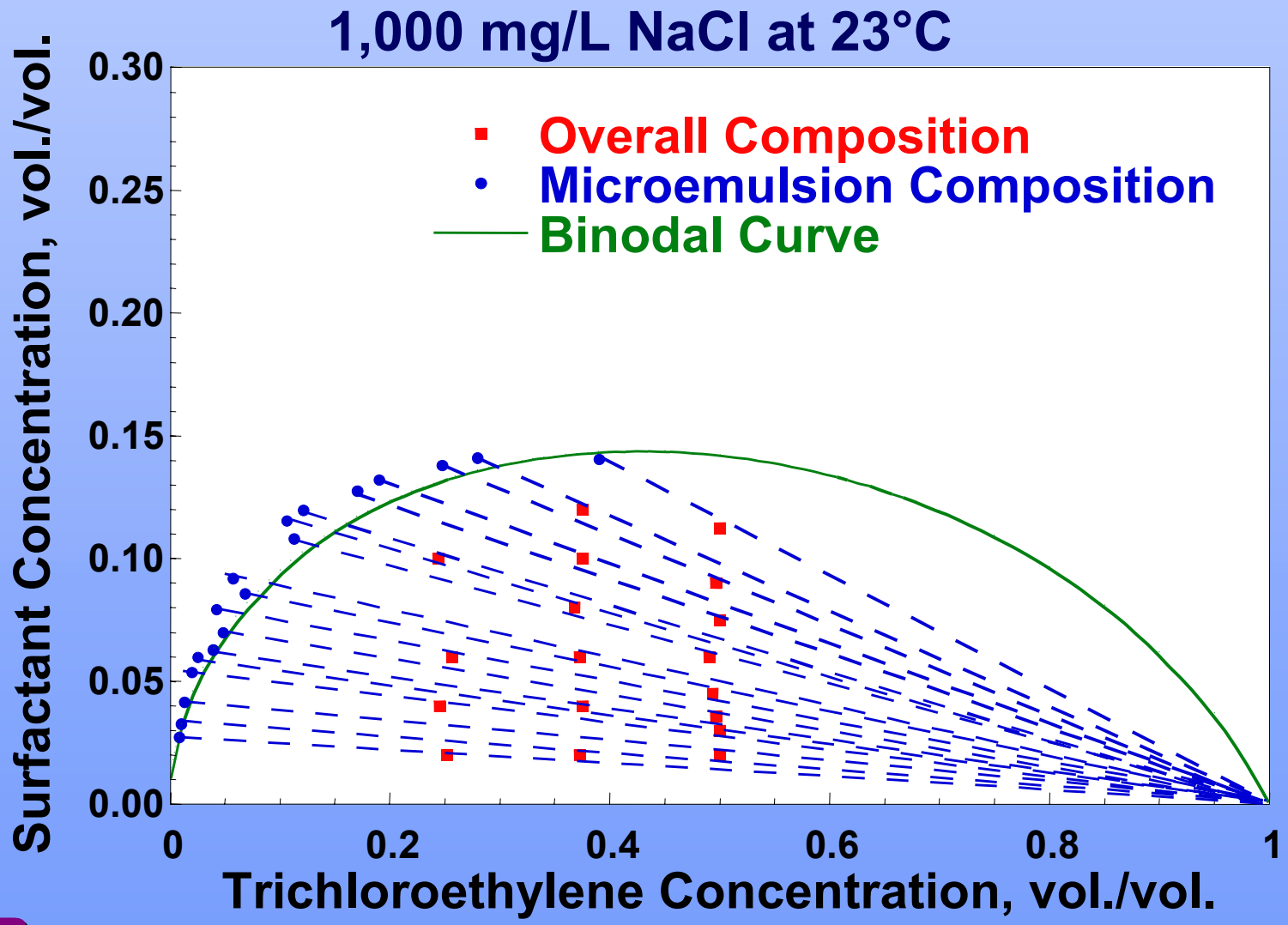
<u>To effect a transition from Type I-III-II</u>

- Increase electrolyte
- Add heavy alcohols
- Reduce temperature
- Increase surfactant tail length

Volume Fraction Diagram



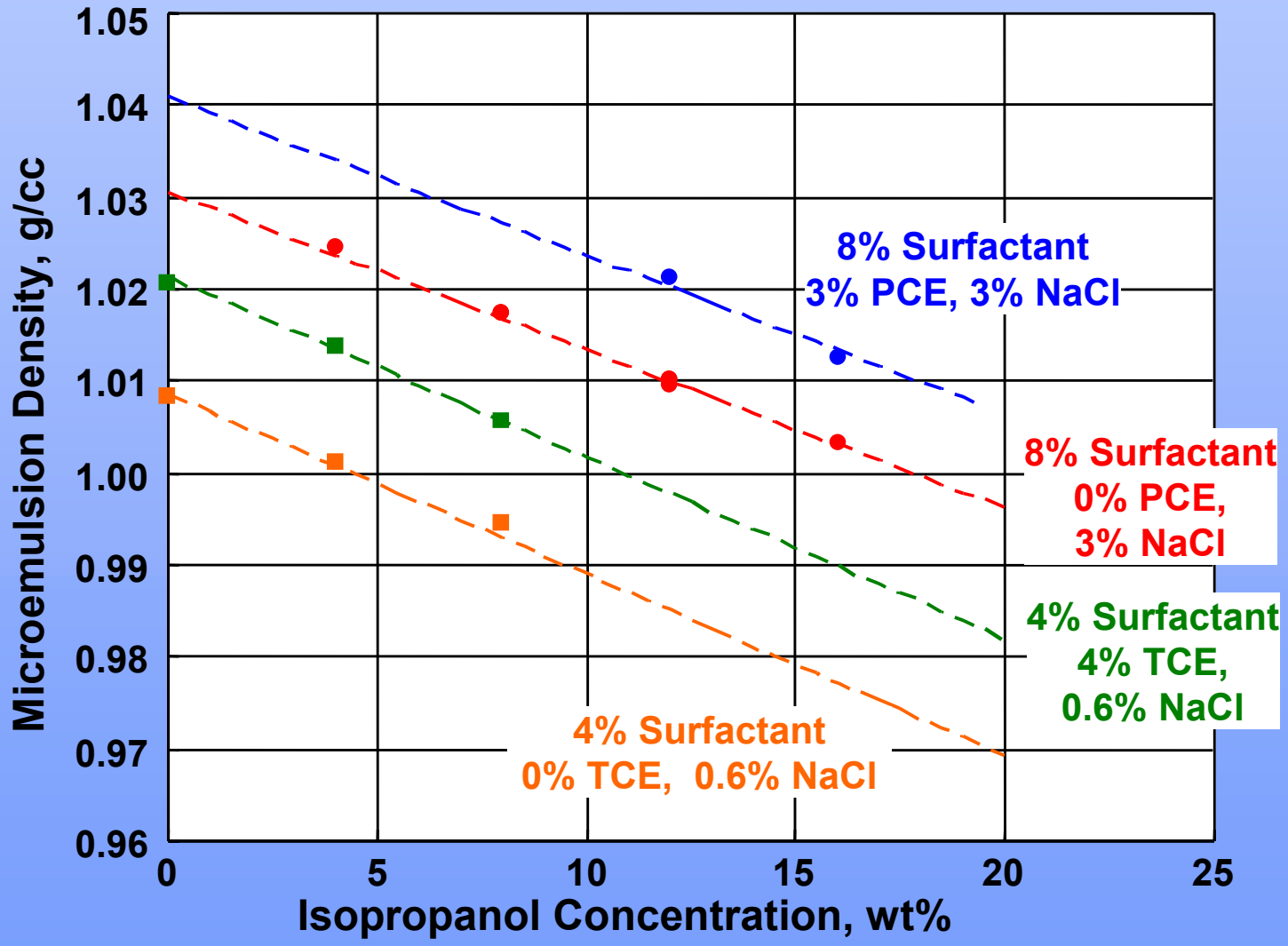
Sodium Dihexyl Sulfosuccinate with TCE



Microemulsion Viscosities

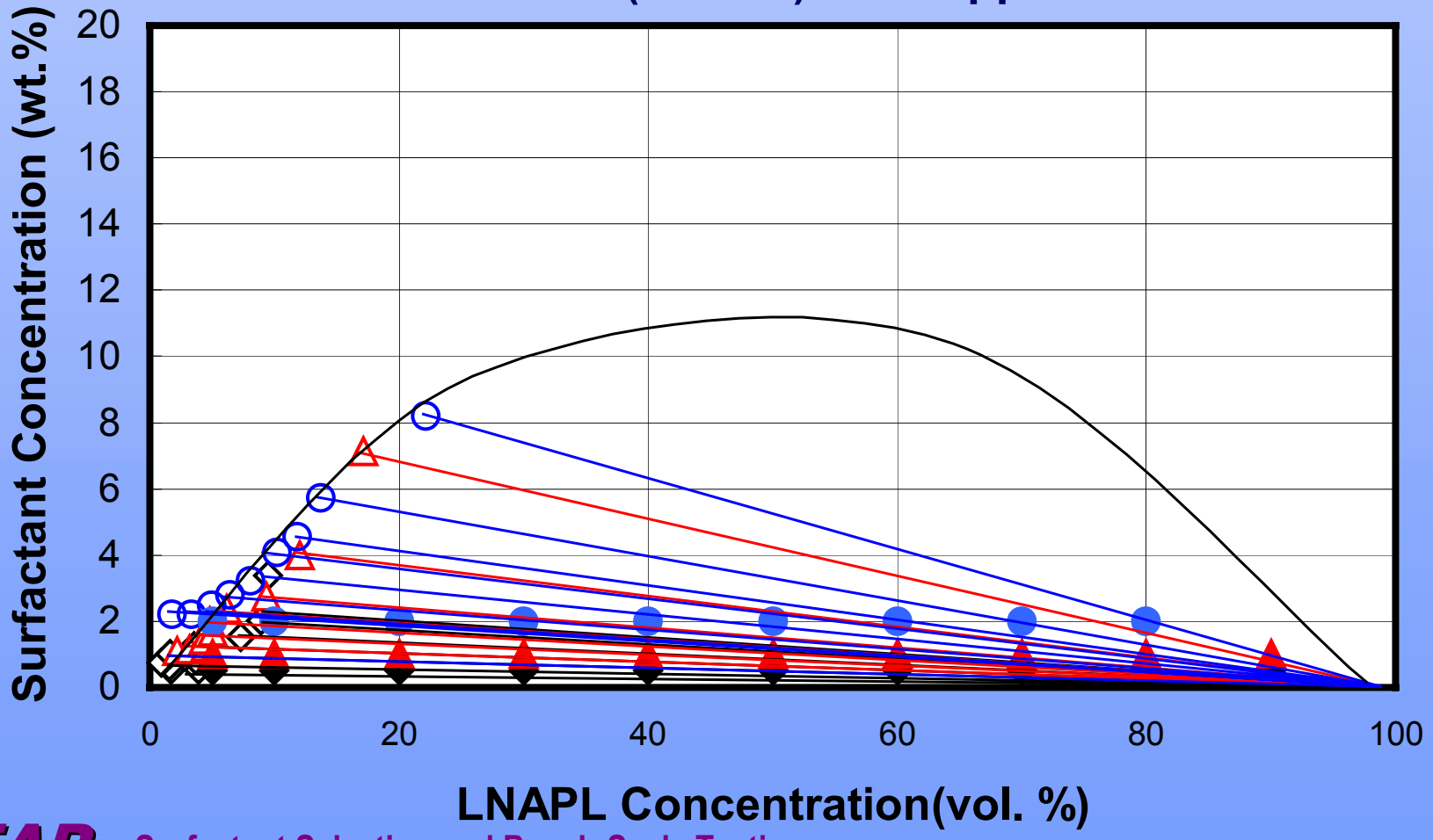
% IPA	NaCl, wt%	Solubilization, mg/L	Viscosity, cp
4	0.67	0	2.6
4	0.5	140,000	5.5
4	0.65	163,000	8.1
4	0.67	257,000	7.9
4	0.69	325,000	7.5
8	0.58	0	2.8
8	0.4	152,000	5.2
8	0.5	178,000	5.3
8	0.55	193,000	7.2
8	0.57	229,000	4.6

Microemulsion Density

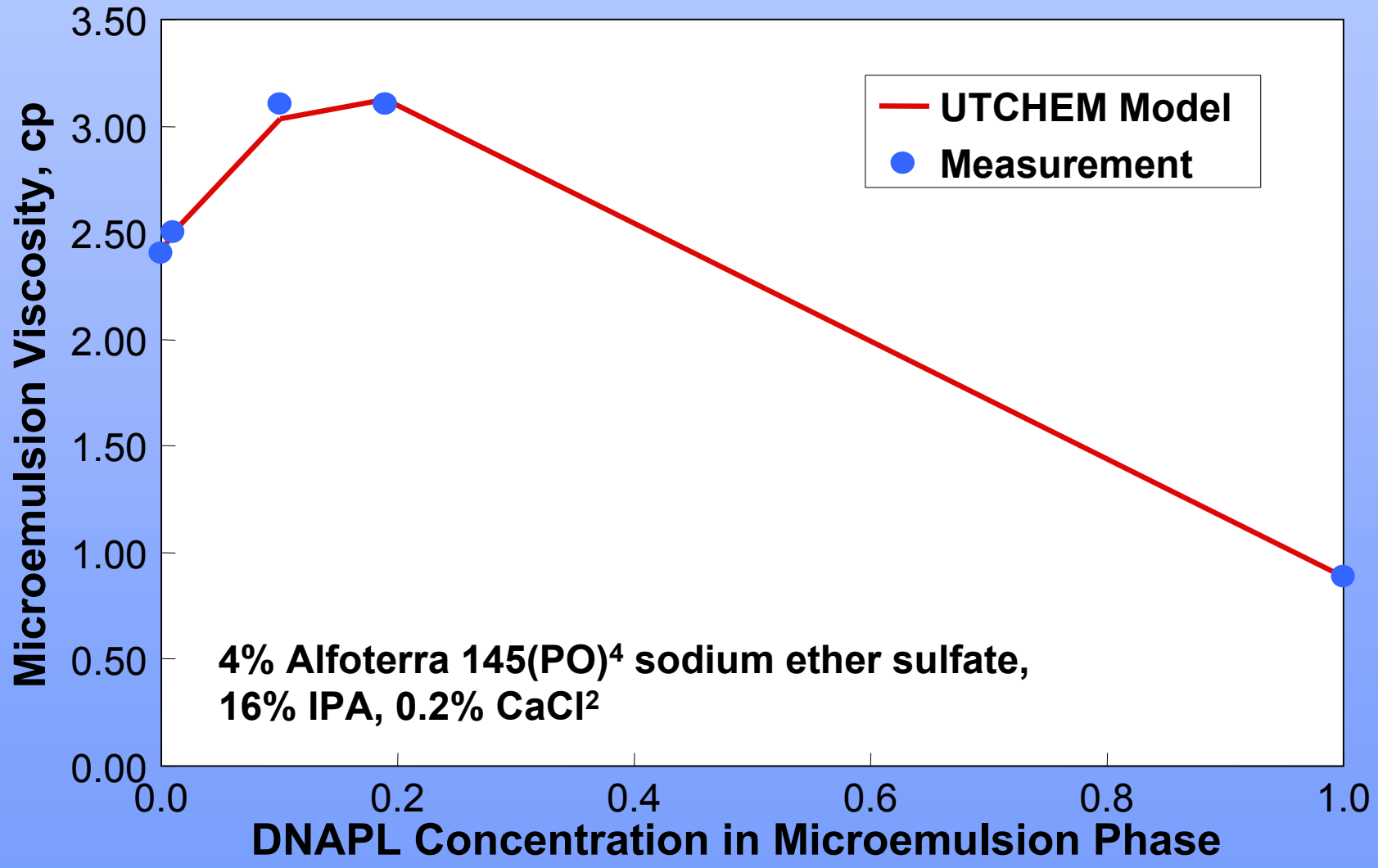


Ternary Diagram

Ternary Diagram Phase behavior of Alfoterra 123-4POSO^{4}Na with Chevron LNAPL (P-I2-45) at 500 ppm Ca++

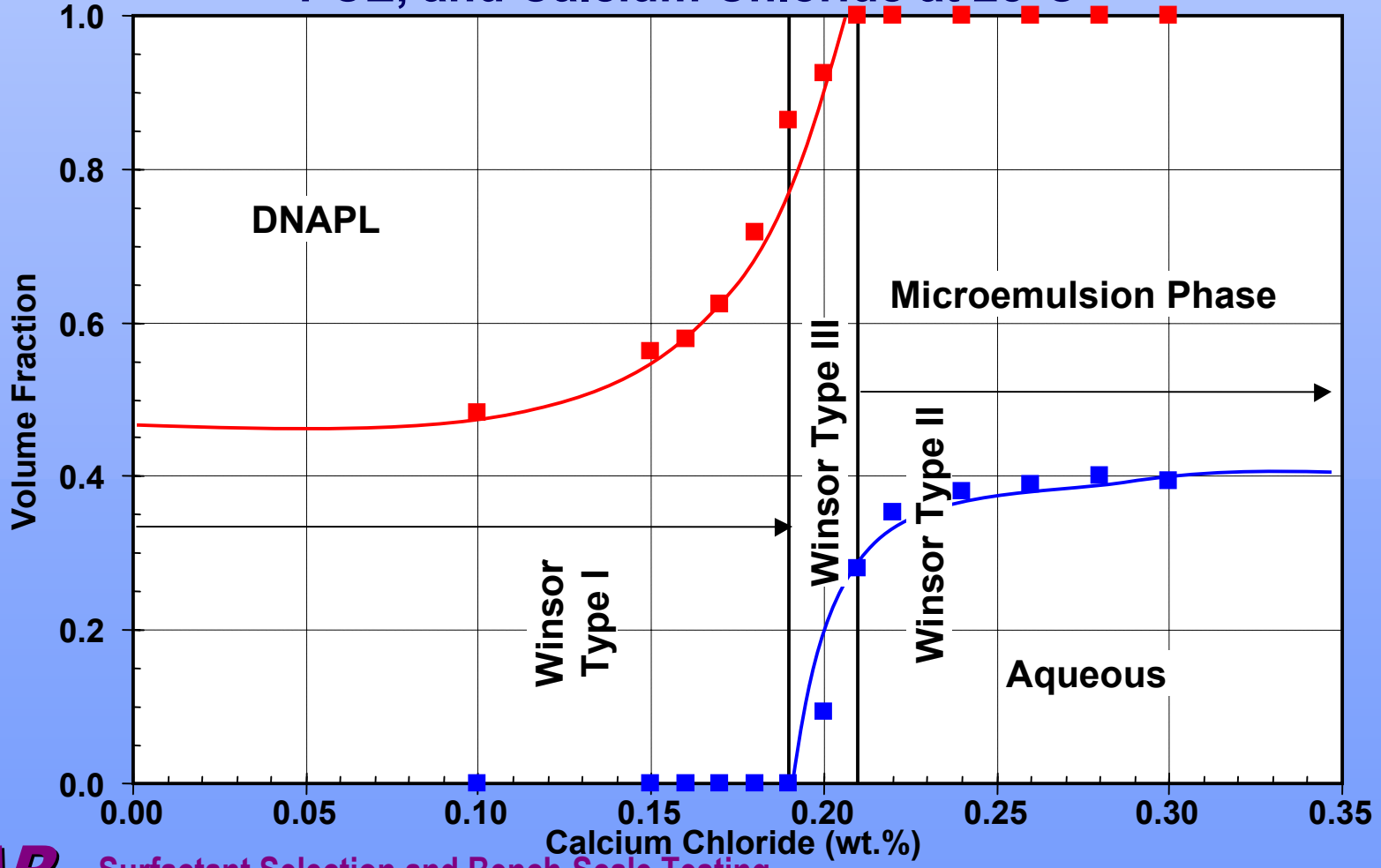


Microemulsion Viscosity

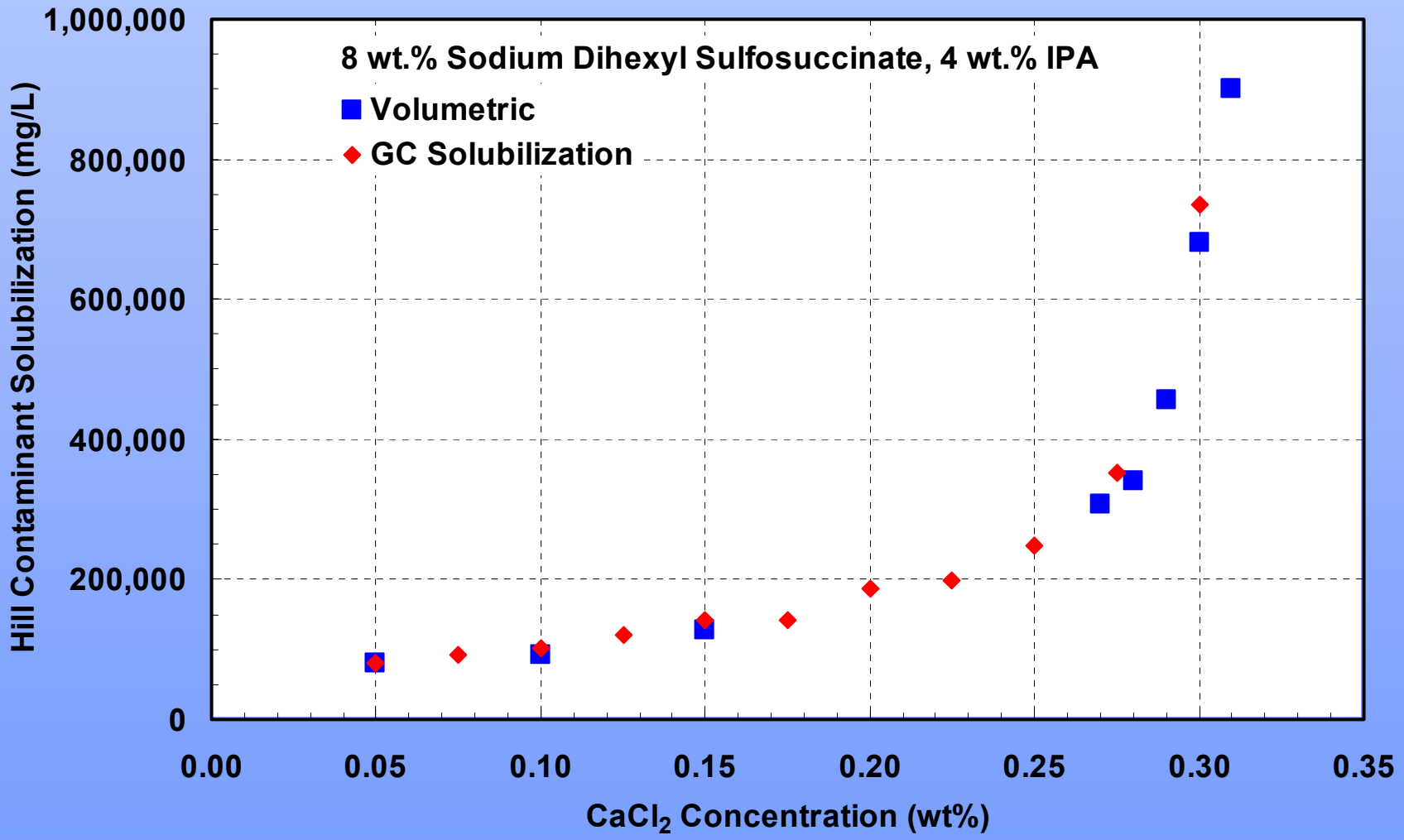


Volume Fraction Diagram

4% by Weight Alfoterra 145-4-PO Sulfate™, 16% by Weight IPA, PCE, and Calcium Chloride at 25°C

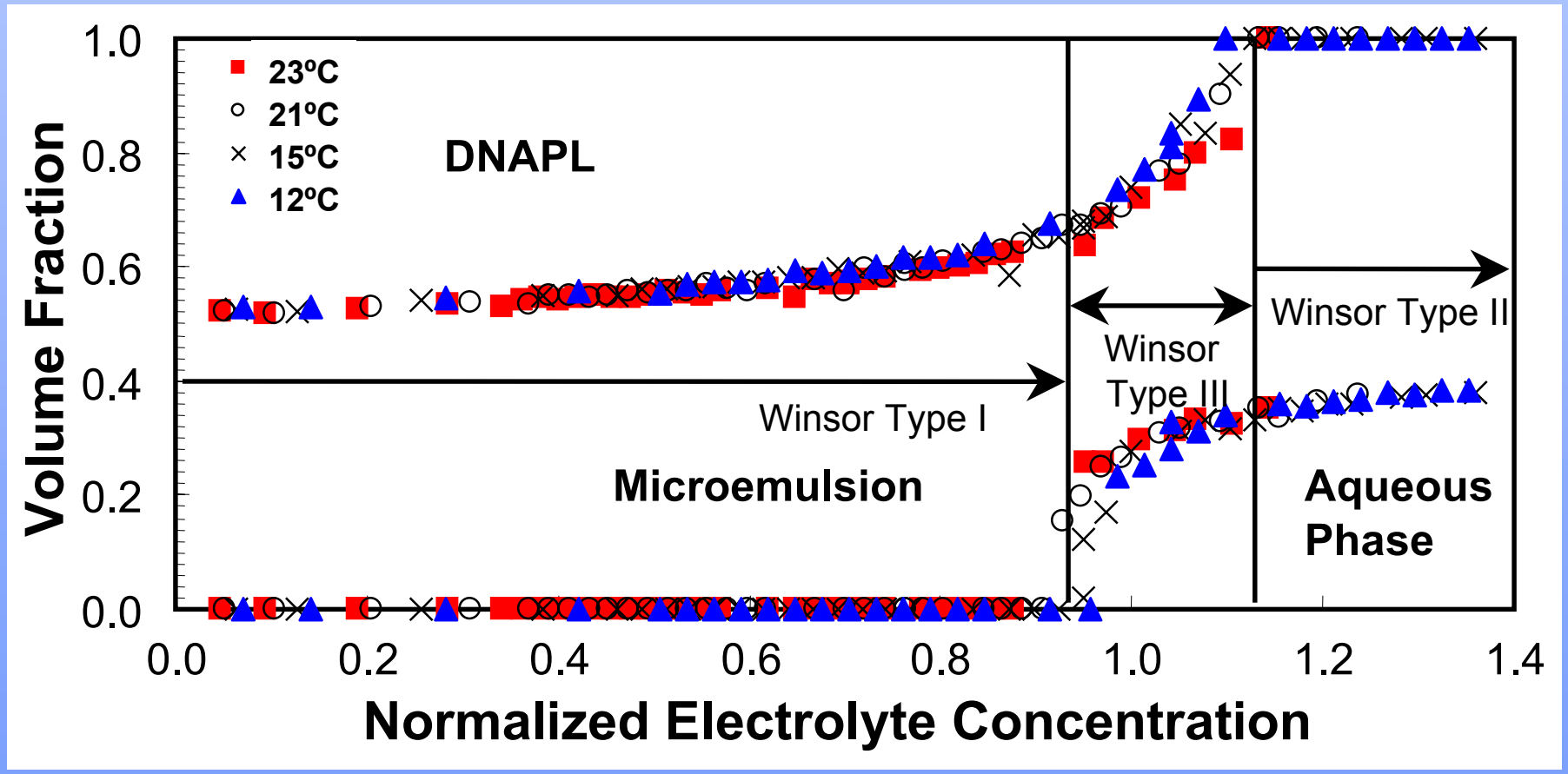


Comparison of GC Measured and Volumetric Estimates of Contaminant Solubilization

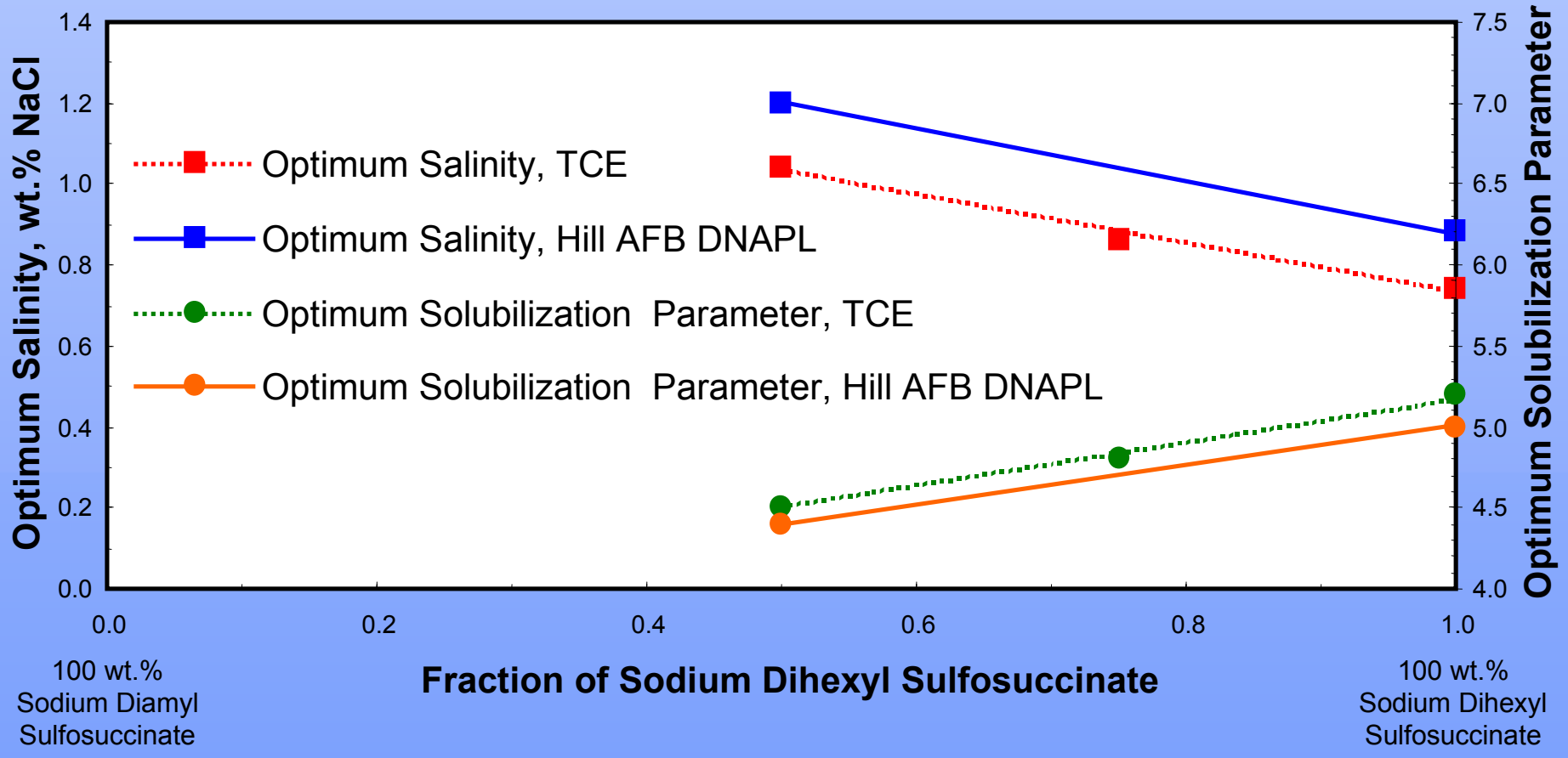


Volume Fraction Diagrams at Different Temperatures

8 wt.% Sodium Dihexyl Sulfosuccinate, 4 wt.% IPA, Hill AFB DNAPL

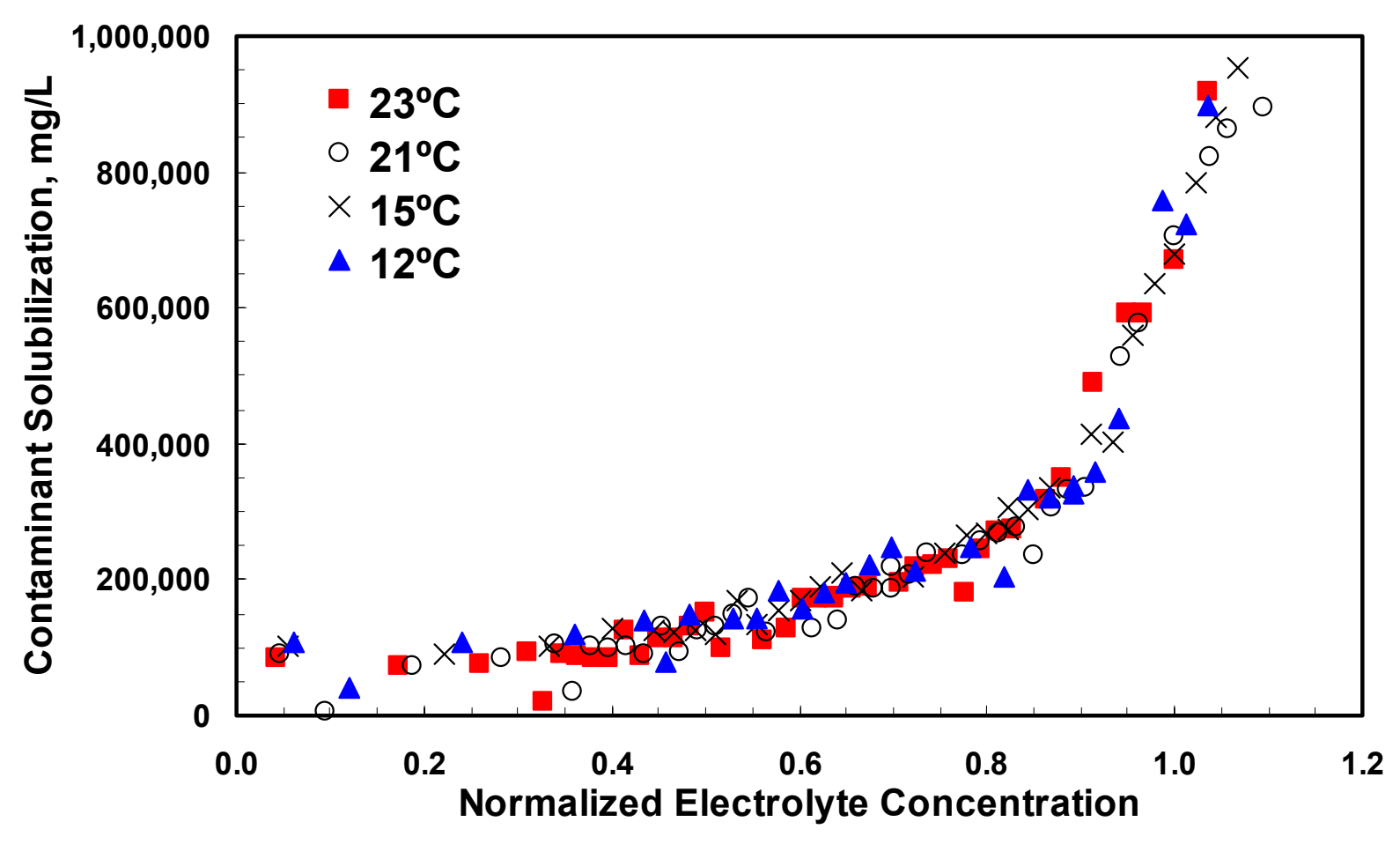


Effect of Surfactant Hydrophobe Length on Optimal Salinity and Optimum Solubilization Parameter

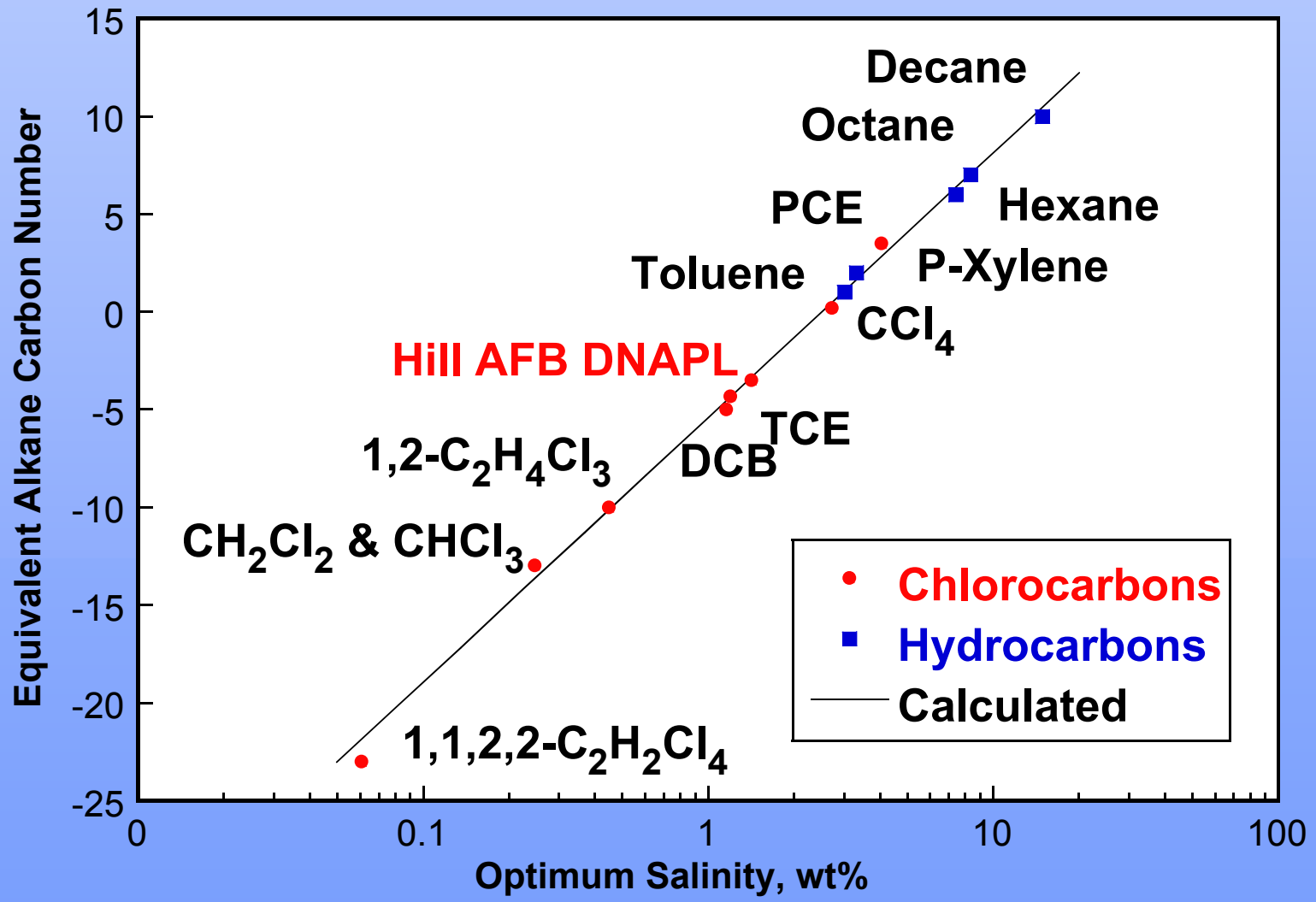


Contaminant Solubilization at Different Temperatures

8 wt.% Sodium Dihexyl Sulfosuccinate, 4 wt.% IPA, Electrolyte, Hill AFB DNAPL



Equivalent Alkane Carbon Number vs. Optimal Salinity



Equilibrium Behavior of Microemulsions

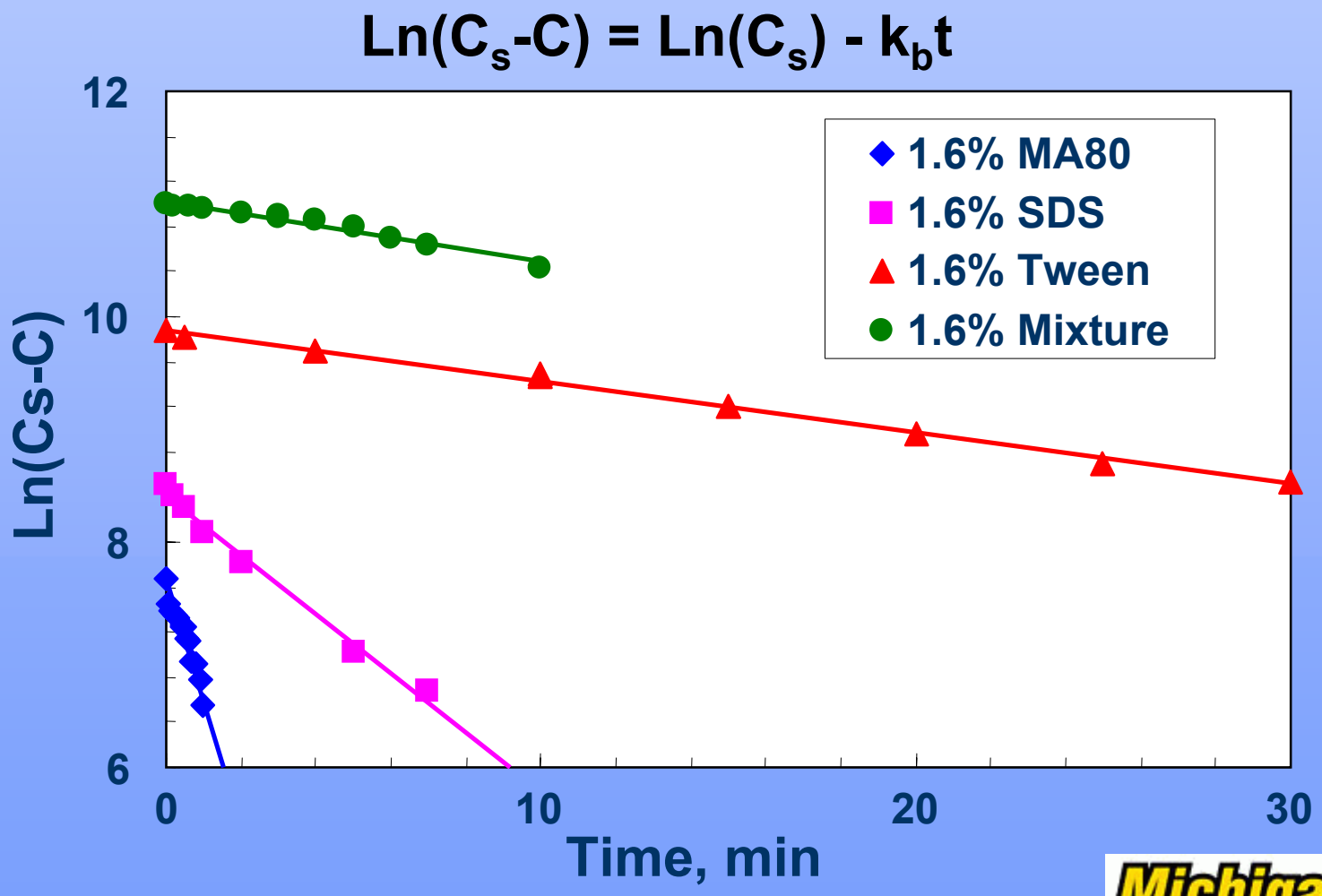
- The most important and widely neglected selection criterion for surfactant solutions is rapid coalescence to a classical microemulsion when mixed with NAPL
- Liquid crystals, gels, and emulsions are common with surfactants and very undesirable because they can cause slow equilibration, high viscosity, plugging, and high retention in the soil

Equilibrium Behavior of Microemulsions (cont.)

- Co-solvents can be used very effectively and inexpensively to eliminate this problem with a good surfactant with a branched hydrophobe
- The phase behavior must be carefully and accurately observed as a function of all pertinent variables, such as temperature and electrolyte content
- When classical phase behavior criteria are met, sorption is so low that it is negligible, and mass transfer is so rapid that local equilibrium on a field scale can be achieved

Non-Equilibrium Processes and Implication

Batch Tests: Effects of Surfactant Type on Kb



Soil Column Results

Final NAPL Saturation

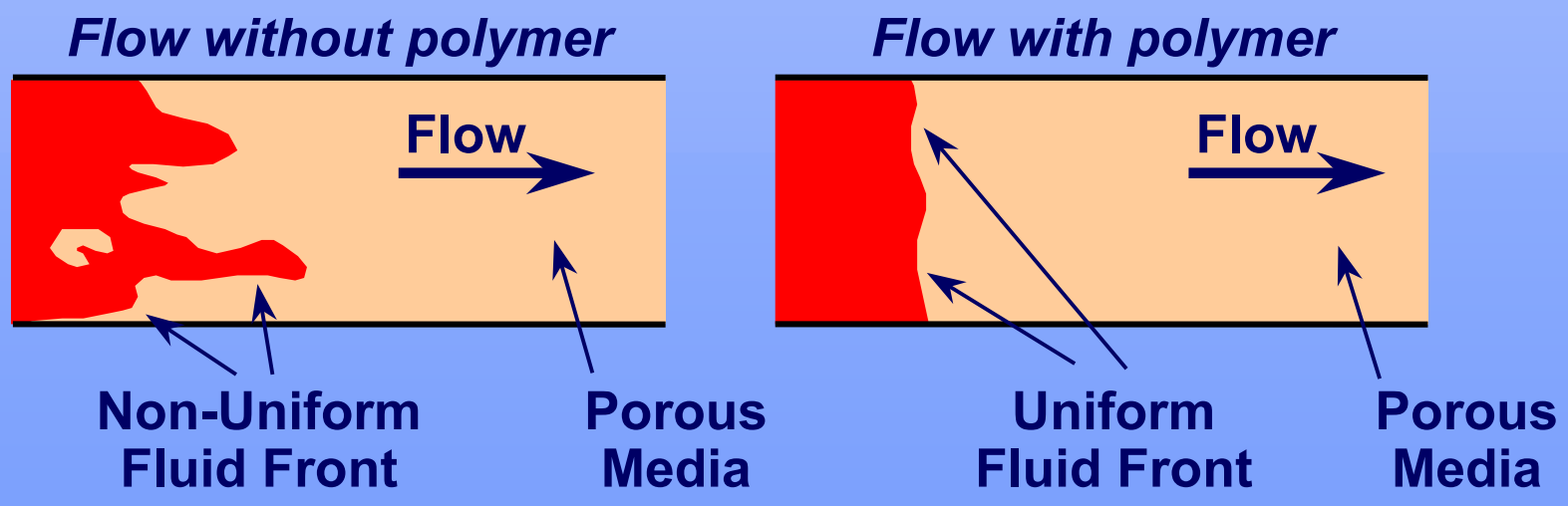
Experiment	NAPL	Mass Balance	Tracers
DW#2	PCE	0.0046	--
DW#3	PCE	-0.0009	0.005
DW#4	TCE	0	0.005
DK1	TCE	0.004	0.016
DW#5	JP4	--	--
JP4#2	JP4	0.023	0.035
DK4	TCE	0.01	0
POLYTCE#1	TCE	-0.0023	0.0001
POLYTCE#2	TCE	0.0038	0.001
POLYTCE#3	TCE	-0.0024	0.0002
HILLOU2#7	DNAPL	-0.0038	0.0002
HILLOU2#8	DNAPL	--	0.0015

Soil Column Results (cont.)

Experiment	NAPL	Initial K Darcy	Final K Darcy
DW#2**	PCE	15.3	1.5
DW#3	PCE	7.3	6.9
DW#4	TCE	8.3	7.1
DK1	TCE	4.5	2.2
DW#5**	JP4	7.1	--
JP4#2	JP4	8.8	8.6
DK4	TCE	6.5	3.2
POLYTCE#1	TCE	5.8	4.9
POLYTCE#2	TCE	4.4	4.2
POLYTCE#3	TCE	6.8	6.2
HILLOU2#7	DNAPL	5.9	4.5
HILLOU2#8	DNAPL	--	7.7

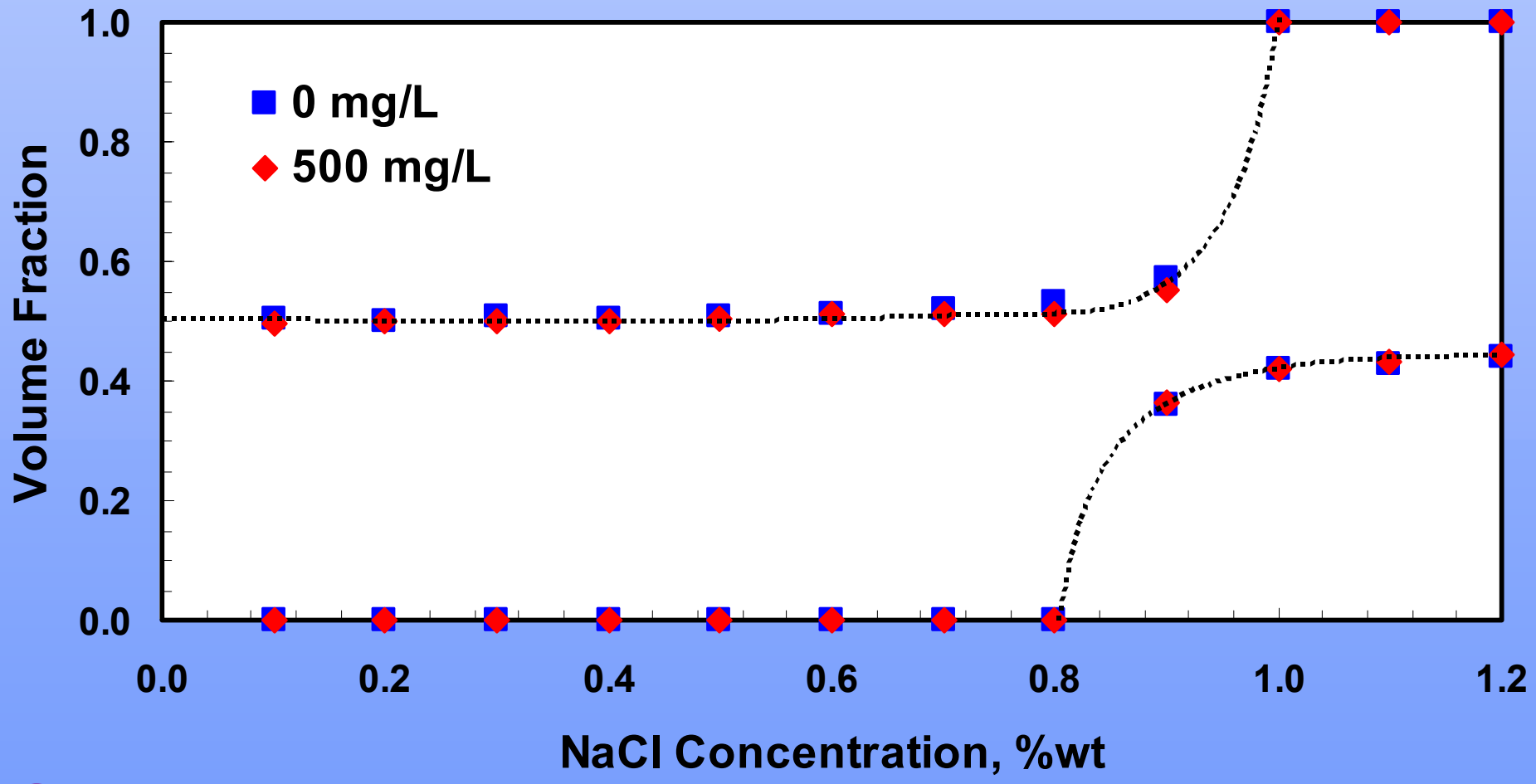
Viscosity Measurements: Mobility Control Using Polymer

- Increases viscosity of surfactant formulation
- Improved sweep efficiency
- Reduce remediation time and amount of surfactant needed for chemical flood

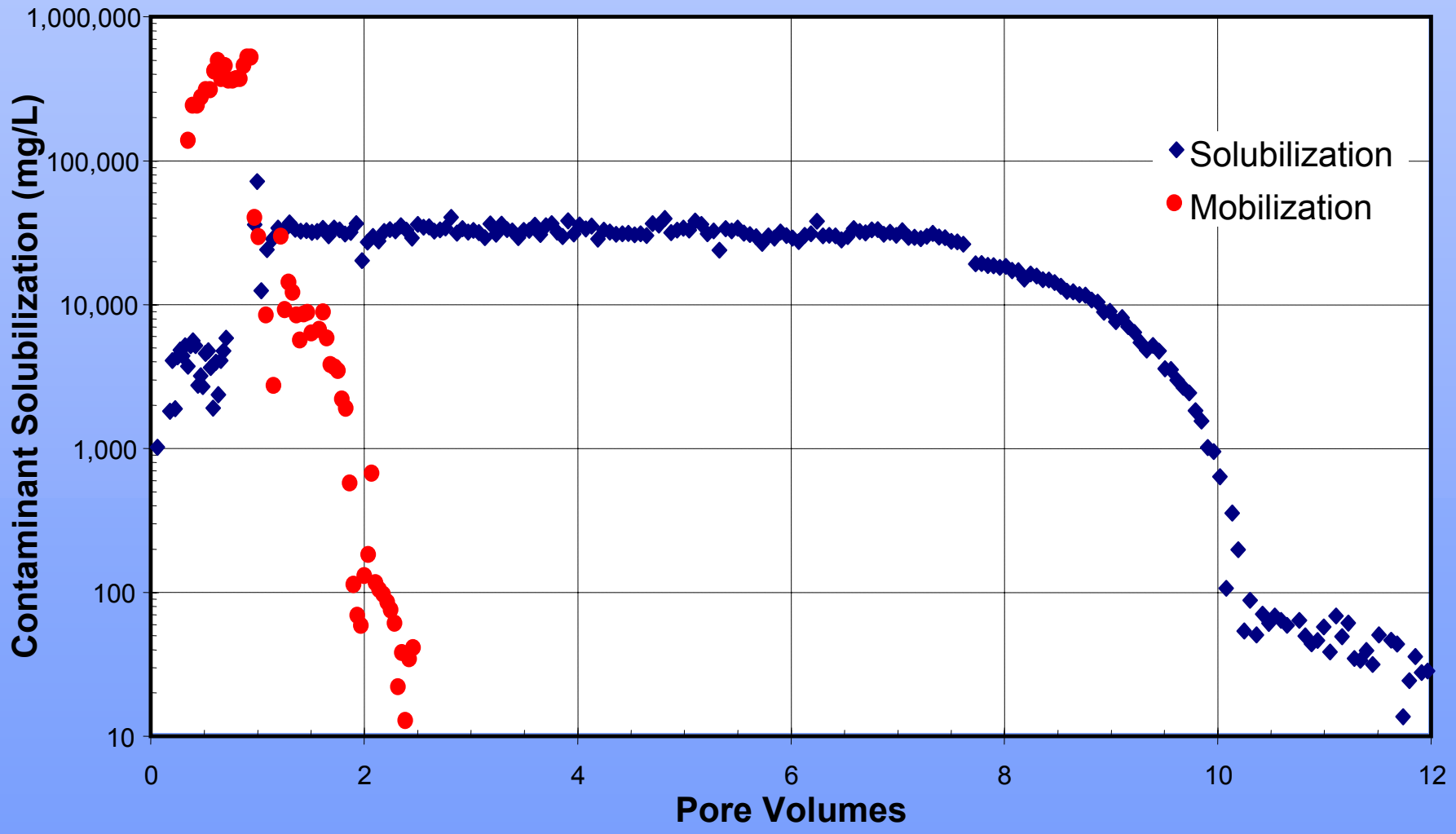


Effect of Polymer on Phase Behavior

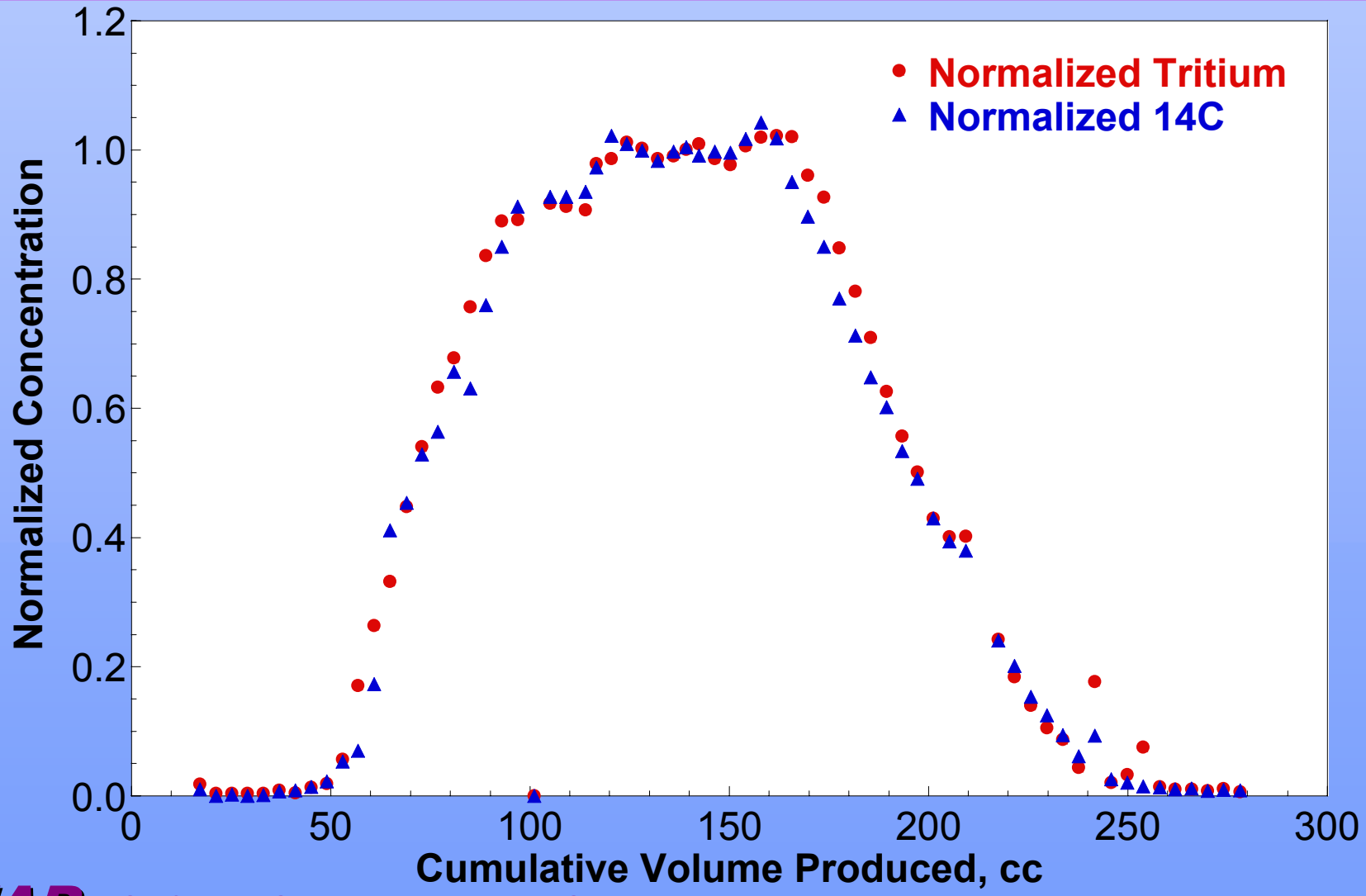
4% Sodium Dihexyl Sulfosuccinate, 8% IPA, Trichloroethylene



Comparison of Solubilization and Mobilization Remediation Regimes



Normalized Tritium and 14C Concentrations for HILLOU2#8



Commercial Availability of SEAR Surfactants

- One size does not fit all
- Commercial production of surfactants for specific SEAR applications requires certain considerations
  - Availability of hydrophobes & intermediates
  - TSCA inventory (PMN's, R&D exemptions)
  - Economics
  - Environmental & safety regulatory questions
- Alfoterra? CONDEA's product line for SEAR
  - Branched alcohol propoxylate sulfates
  - Tailored for contaminant and site conditions
  - MCB Camp Lejeune, Naval Station Pearl Harbor, future use at other sites

Effects of Surfactant Structure on Biodegradation

- The concept of biochemical infallibility (what Nature synthesizes, Nature also degrades): ability to degrade surfactants is related to their structures/chemical groups being analogous to natural substances
  - Branching of hydrophobe decreases biodegradation rates
  - Propoxylation decreases biodegradation rates compared to equivalent degrees of ethoxylation
  - Sulfonates (carbon to sulfur bond) are more difficult to break than sulfates (carbon to oxygen to sulfur bond)
  - Ester linkages between hydrophobe and hydrophilic groups are easily broken

Effects of Surfactant Structure on Biodegradation

- Biodegradation requiring oxidative attack (e.g., oxygenase activity) will not occur readily in anoxic subsurface environments (e.g., LAS, Dowfax?)
- Desirable that biodegradation intermediates exhibit less microbial toxicity than the parent compound (alkyl phenol ethoxylates are examples of this problem)
- Purposeful design of a SEAR surfactant to maximize biodegradation may result in a poor performer: **Balance between performance and biodegradation is important**

Treatability Above-Ground

- To recycle or not to recycle……...?
- Above-ground surfactant treatment technologies that directly or indirectly relate to surfactant structure
  - Micellular enhanced ultrafiltration (MEUF): CMC is important
  - Biological treatment
  - Surfactant precipitation
  - Chemical destruction: hydrolysis, oxidation (requirement for labile groups)
  - Phase separation

Conclusions on Structure vs. Performance

- Use of anionics (do not sorb as much to sediments)
- Soluble at concentrations & temperature of SEAR (nature of hydrophile is important)
- Matching hydrophobe with NAPL contaminant (e.g., HLB)
- Surfactants that disrupt structure are best for microemulsions of NAPL (e.g., branching, PO)
- Ability to tailor surfactants is useful

It is essential that optimization of surfactant for performance does not create another environmental problem.

Summary and Conclusions

- SEAR is a very viable technology in remediating NAPL-contaminated soils
- If the proper screening techniques for surfactant selection are used residual NAPL saturations as low as 0.03% can be achieved in both lab and field tests
- New advances have allowed us to custom-design surfactant molecules for specific contaminants

Any Questions?

SEAR