

Surfactants

Gary A. Pope

**Workshop on Heavy Oil Recovery
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The University of Texas at Austin

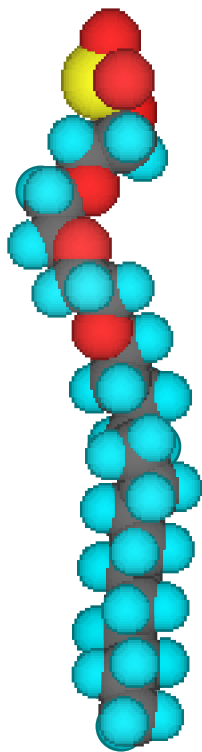
Background on Surfactant EOR

- Extensive research and development was done on surfactant EOR in the 60s, 70s and 80s including many field pilots
- By the mid 80s surfactants had been developed with high salinity tolerance and other characteristics far superior to the earlier products
- By the mid 90s surfactant structure could be tailored to the specific conditions needed
- The surfactant cost is on the order of \$10 per incremental Bbl of oil
- The use of alkaline agents such as sodium carbonate with surfactants can reduce chemical costs to less than \$5 per Bbl of incremental oil in some cases and this has been applied commercially on a limited scale, but is limited to certain reservoir conditions

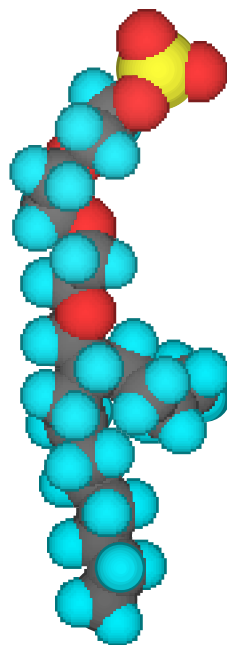
Background on Surfactant EOR

- Many pilot tests done in the 1970s did not adequately recognize the importance of reservoir characterization and mobility control
- Oil recovery is usually very low without mobility control
- Under favorable conditions, either hydrolyzed polyacrylamide or xanthan gum polymers can be used for mobility control, but both have limitations
- Our capability to simulate surfactant flooding with UTCHEM has continued to improve and is vastly better than it was during the 1970s and 1980s
- The limitations of most surfactants is usually related to high viscosity emulsions or microemulsions and high retention
- The key to reducing both viscosity and surfactant retention is the same: surfactant structure with special emphasis on branched hydrophobes

Examples of Alcohol Ether Sulfate Surfactants

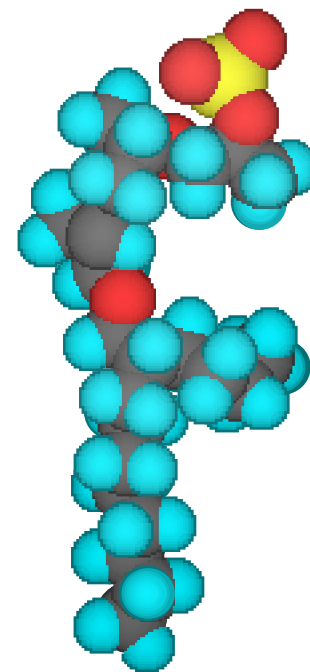


C14 EO3-sulfate
(linear alcohol)



C14 EO3-sulfate

(C4 branch at the #2 carbon)

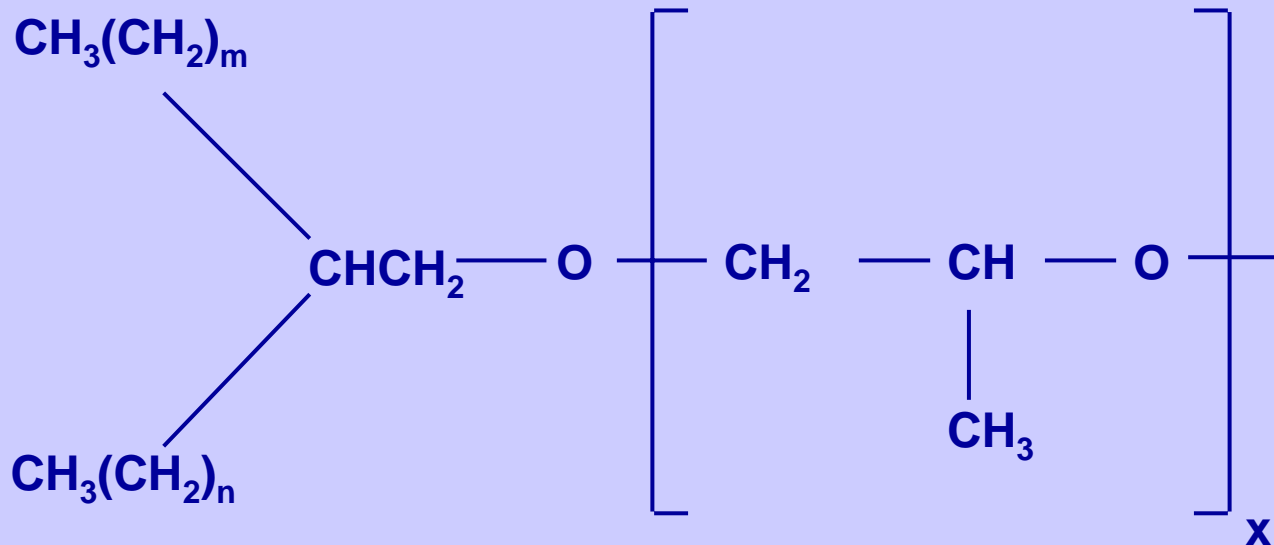


C14 PO3-sulfate

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

Custom Designed Surfactant

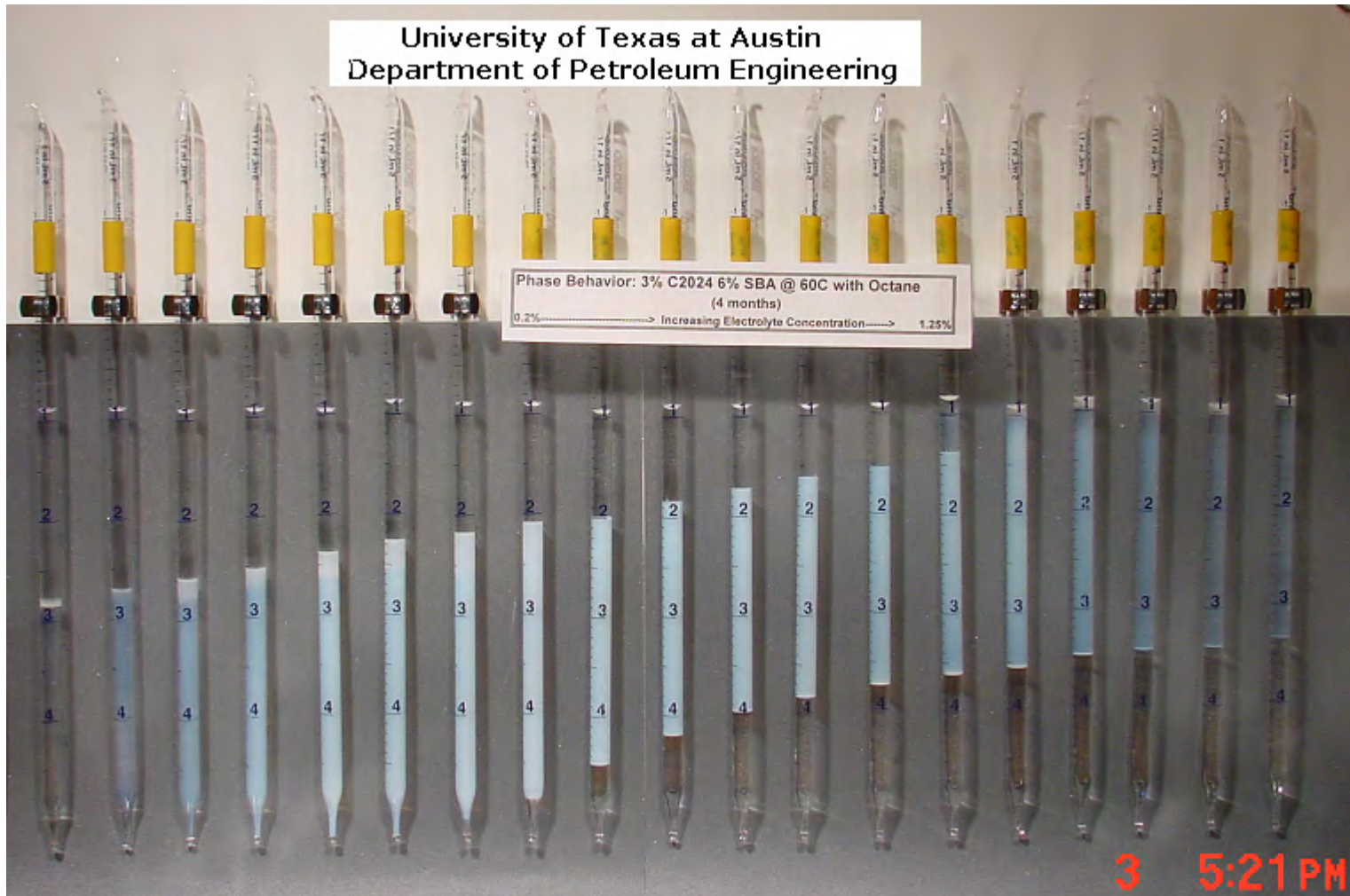
Hydrophobic Tail



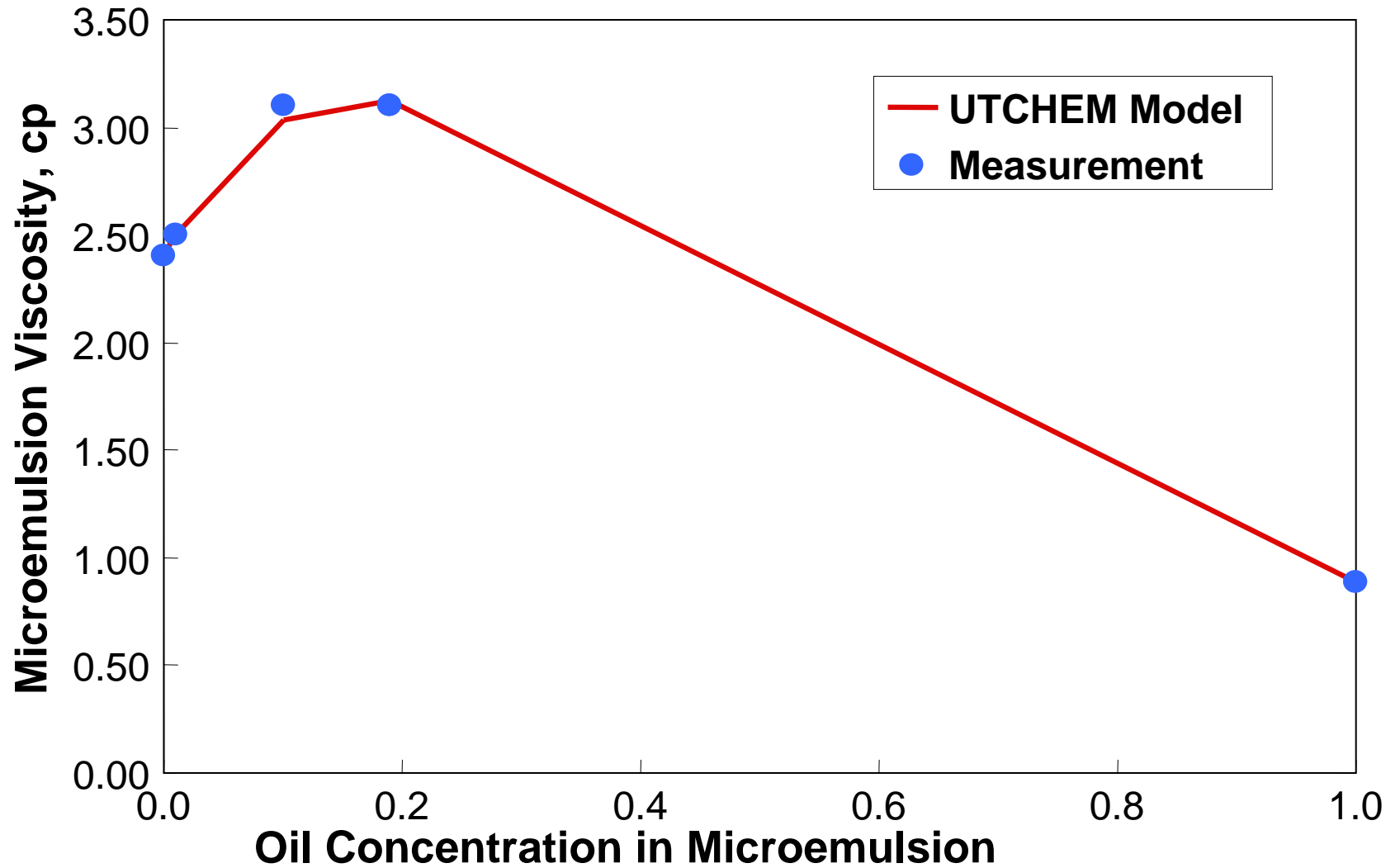
Hydrophilic Head

Where $m+n$ = Desirable hydrophobe tail

Microemulsion phase behavior



Microemulsion Viscosity



Examples of Commercial Surfactants for EOR

- **Stepan**
 - Alpha Olefin Sulfonates C14 C1618 C2024
 - Alcohol Ether Sulfates C13 C1618
- **Harcros**
 - Alcohol Ether Sulfates C12 C13
- **Sasol**
 - Alcohol Ether Sulfates C12 C16 ...
- **Shell Chemical**
 - Internal Olefin Sulfonates C15-C17
- **Cytec**
 - Ester Sulfonate C12...
- **Oil Chem**
 - Alcohol Ether Sulfonates C14...

Example of Current Surfactant/Solvent/Polymer Mixture for EOR of Light Oil in Dolomite Reservoir

- **Surfactant mixture**
 - **C16-17Alcohol Propoxy Sulfate (APS) with 7 POs**
 - **C20-24 Alpha Olefin Sulfonate (AOS)**
 - **Secondary Butyl Alcohol (SBA)**
- **Hydrolyzed Polyacrylamide Polymer (HPAM)**

Phase Behavior Screening

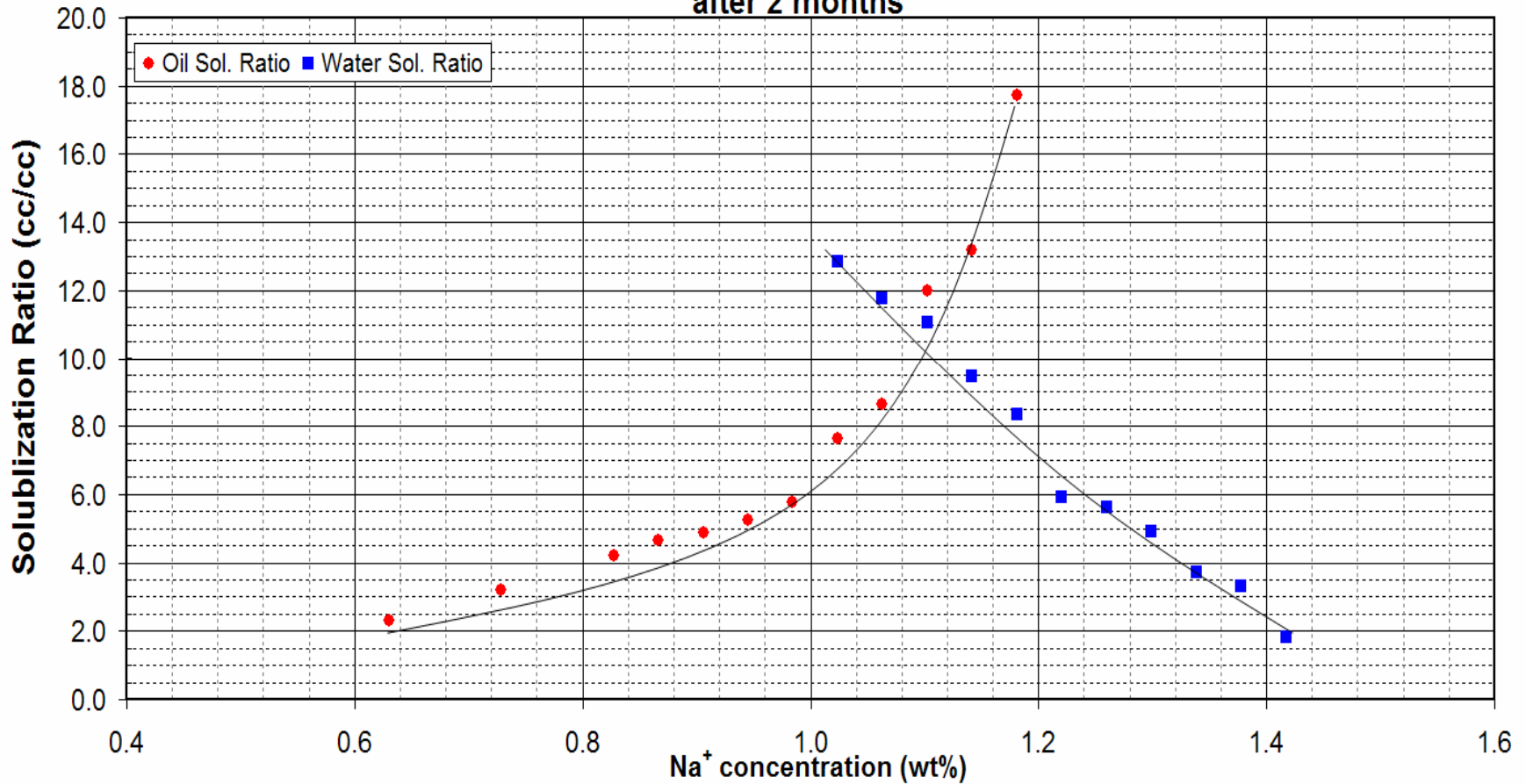
An optimum formulation of APS/AOS/SBA with polymer

Increasing Na^+ Conc. \longrightarrow



Solubilization Ratios

Solubilization vs Na⁺ concentration
2% active APS C16-17/AOS C20-24/SBA mixture with Midland Farms crude
after 2 months



Summary

- **Phase behavior screening method allows rapid design of surfactant flood systems**
- **Oil recovery in both sandstone and dolomite cores about 90%**
- **Surfactant adsorption in dolomite core similar to sandstones**

Example of Successful Recovery of Viscous Fuel Oil at Pearl Harbor Site

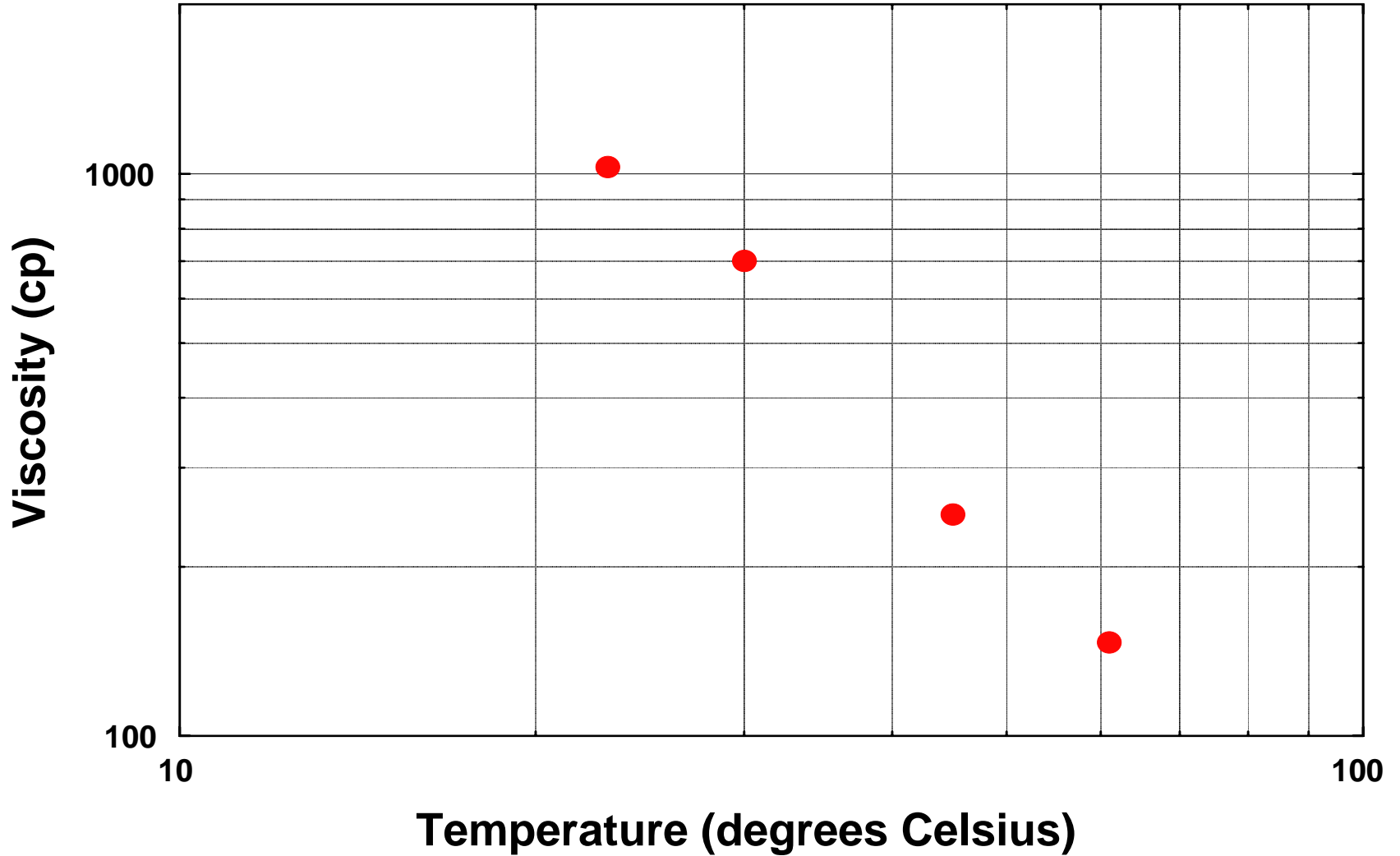
Background

- **High viscosity oil**
 - **1000-3000 cp**
 - **Commercially-available surfactants gave very poor solubilization of the NSFO**
 - **No published data on how to use surfactants for 1000 cp oils**
- **Complex hydrogeology**

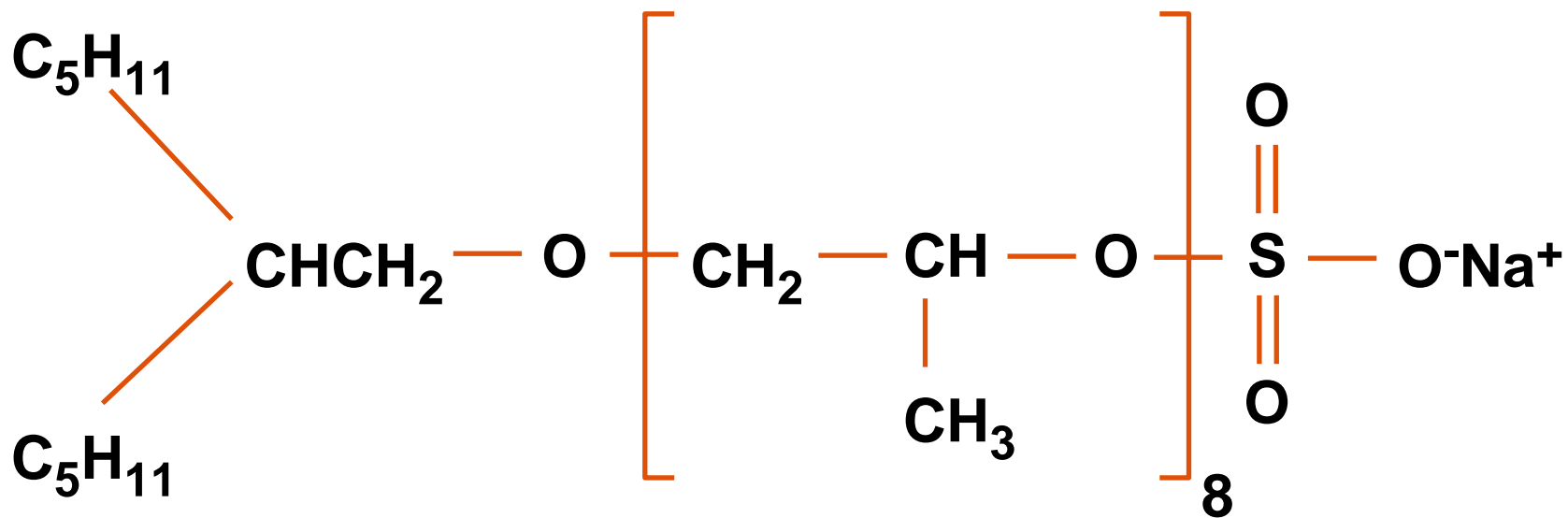
Hydrogeology



Viscosity of Fuel Oil



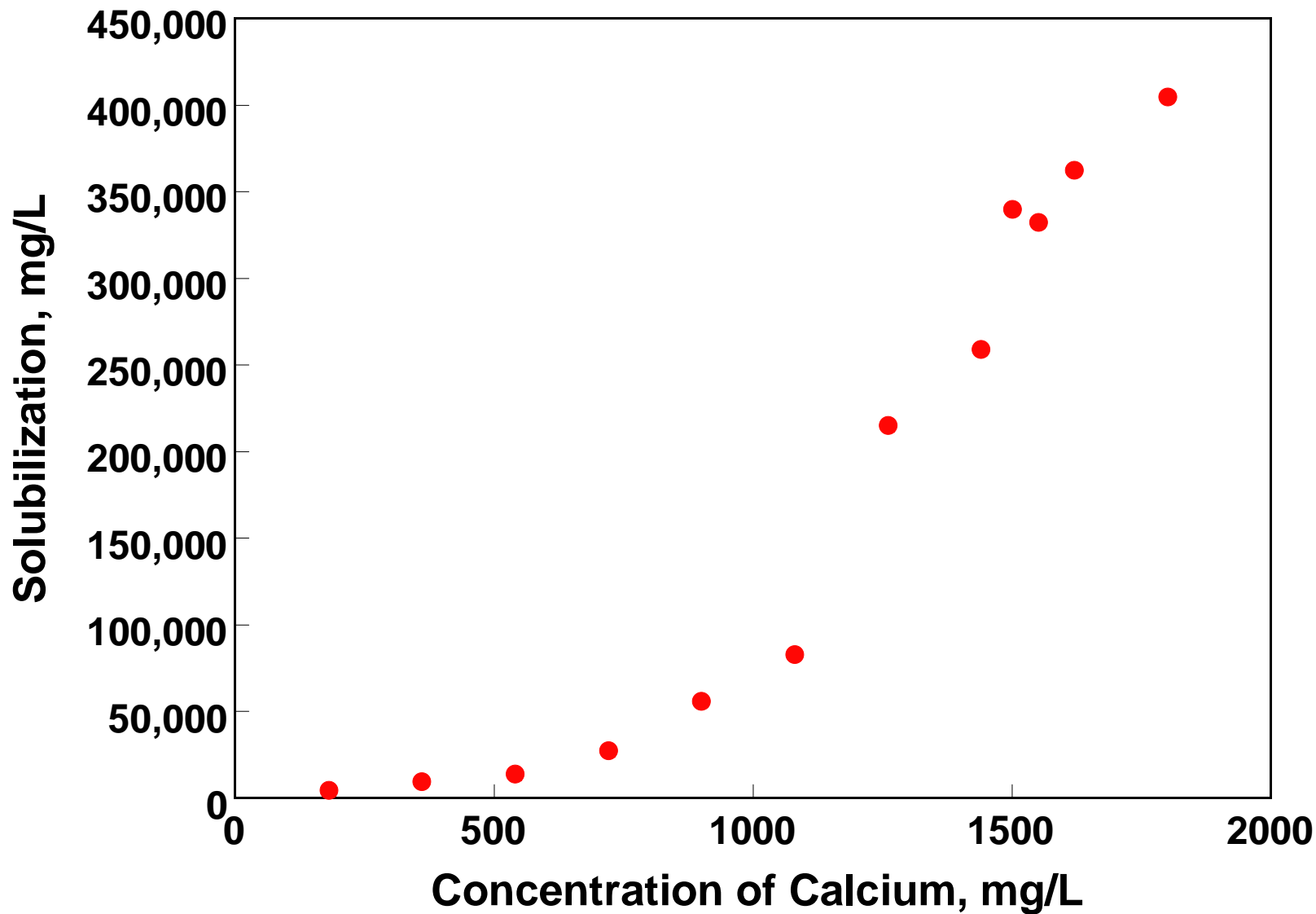
Approximate Structure of Sodium Alkyl Propoxylated Sulfate



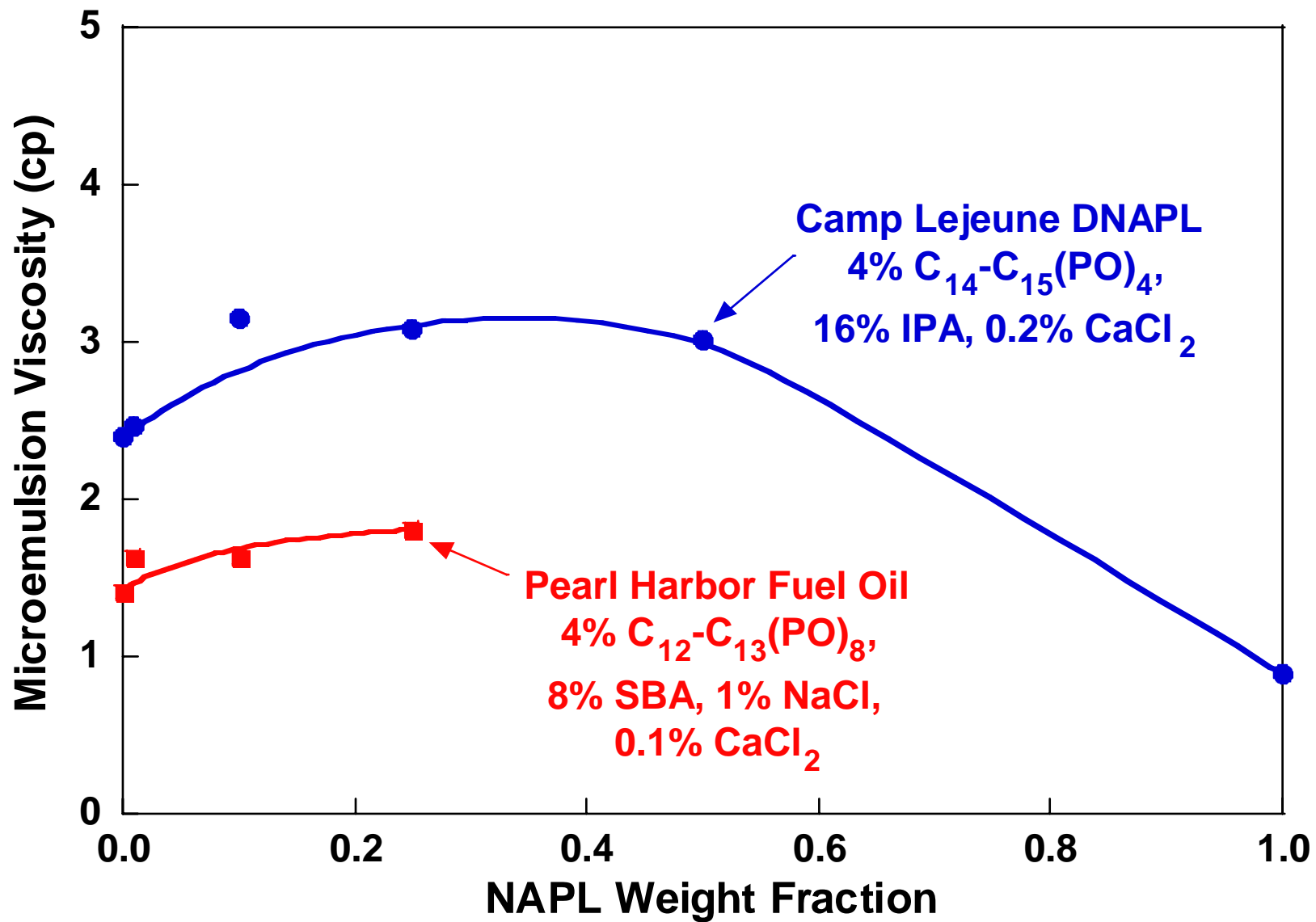
Sodium Alkyl Propoxylated Sulfates

- **Robust high-performance surfactants**
- **Low viscosity microemulsions**
- **High contaminant solubilizations**
- **High tolerance to calcium**
- **Favorable biodegradation properties**

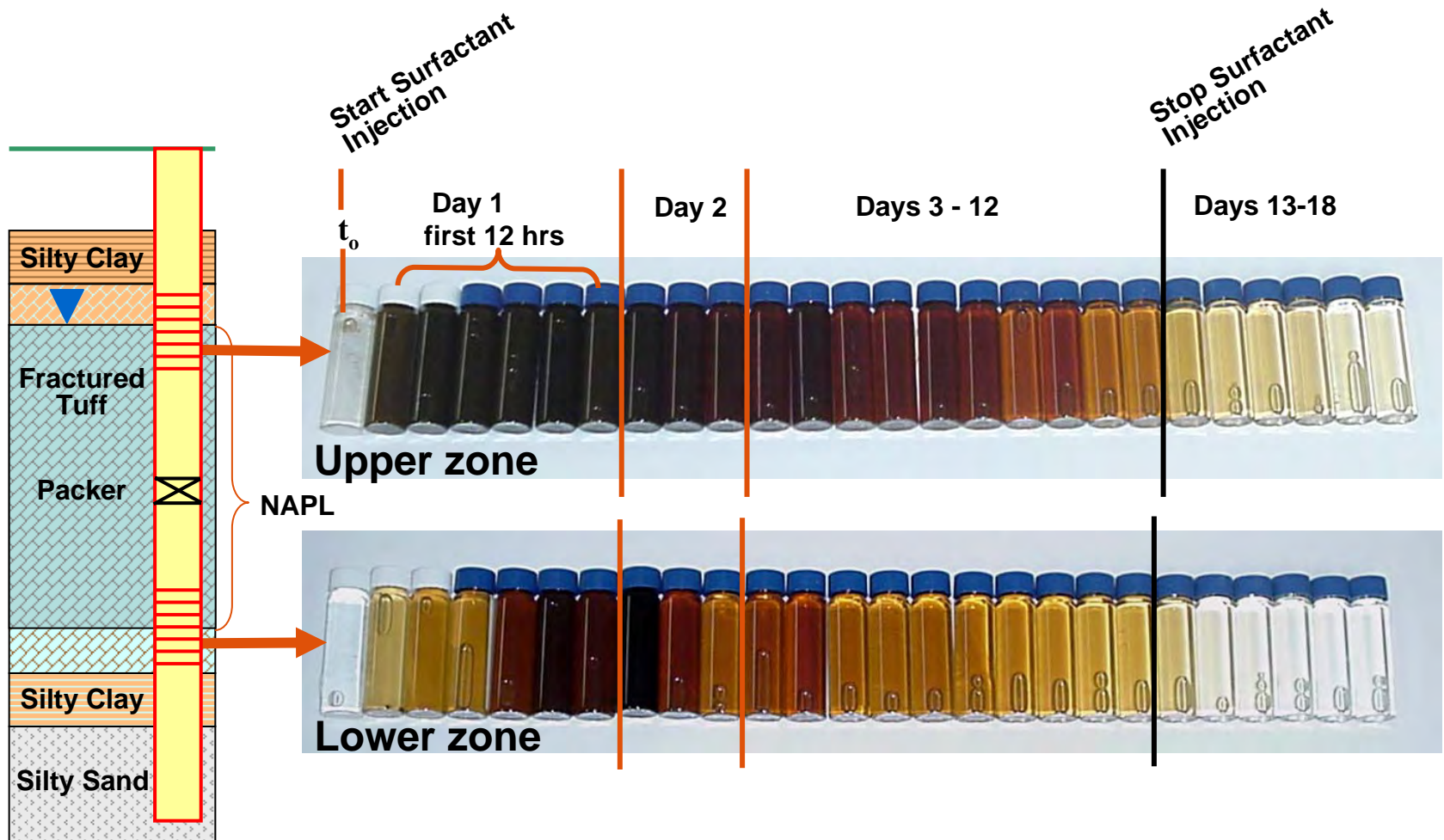
Solubilization of Pearl Harbor Fuel Oil at 50°C



Microemulsion Viscosity



Effluent Samples Collected During Surfactant Flooding at Pearl Harbor



Summary of Pearl Harbor Results

- **Phase behavior and viscosity measurements effective in identifying high-performance surfactants for recovery of highly viscous fuel oil**
- **Alkyl propoxylated surfactants found to be a robust and cost-effective class of surfactants**
- **Thermally enhanced SEAR tested in laboratory and field to remove 1000 cp fuel oil**
- **Approximately 88% of viscous fuel oil removed from fractured tuff at Pearl Harbor**

Proposal

Enhancement of Mass Transfer in Heavy Oil Recovery Processes using Surfactants, Solvents, Alkali and Heat

- **Custom design surfactant structures for heavy oil**
- **Explore novel recovery methods with surfactants**
- **Develop models of both microscopic and macroscopic phenomena as needed to understand and scale up mechanisms**