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# Novel Methodology for the Highly-Efficient Separation of Oil and Water

**16 March 2014**


**Joseph Mabry, Anish Tuteja, Andrew Guenthner, Josiah Reams, Arun Kota, Gibum Kwon, Wonjae Choi**
**Air Force Research Laboratory**
**Aerospace Systems Directorate**
**joseph.mabry@us.af.mil**
**(661) 275-5857**



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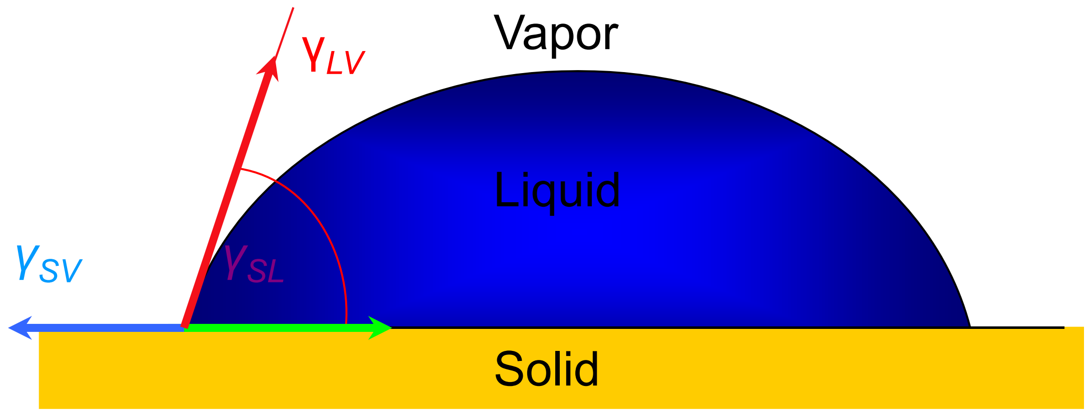
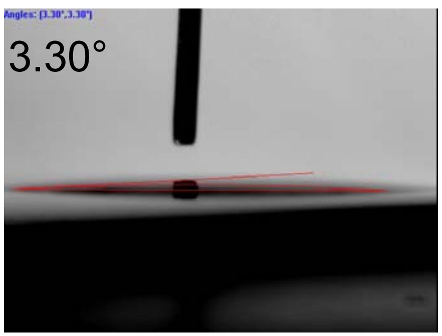
# Non-wetting surfaces

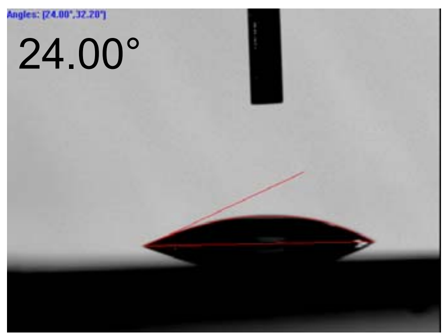



Contact angles with water:



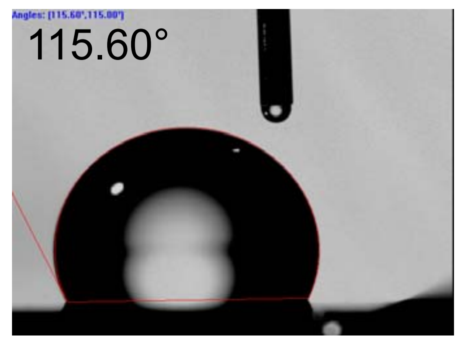

Superhydrophilic

$\theta \sim 0°$



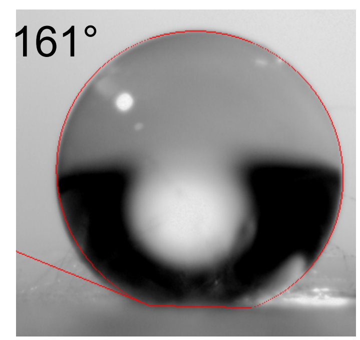

Hydrophilic

$0° < \theta < 90°$




Hydrophobic

$\theta > 90°$




Superhydrophobic

$\theta^* > 150°$

Similarly, superoleophobic surfaces display contact angle $\theta^* > 150°$ with oils or alkanes

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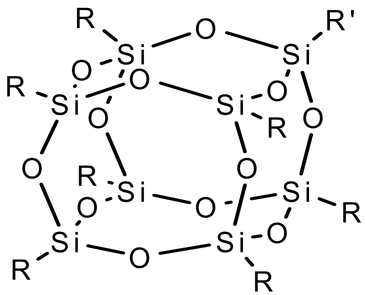
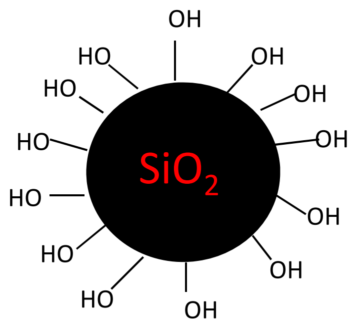
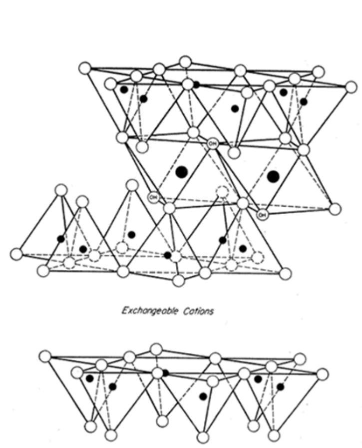
# Nanocomposite Materials



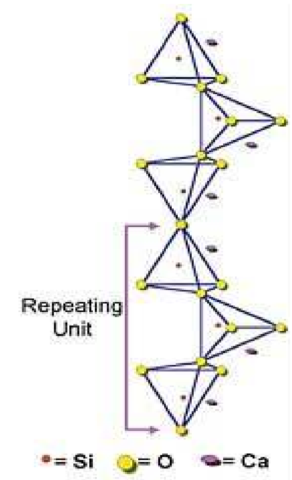
**POSS**



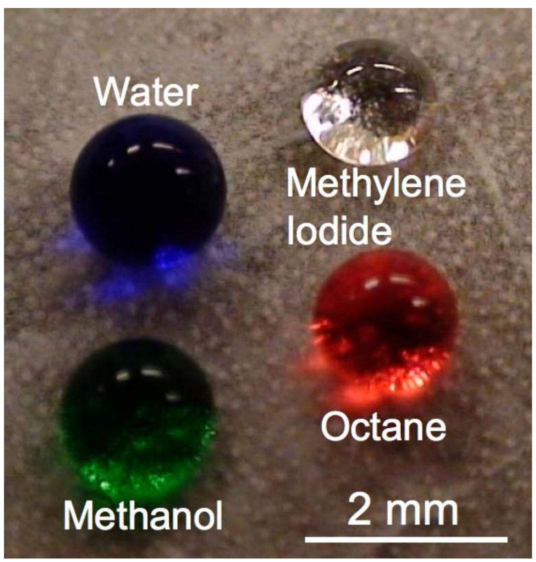

**Nanosilicas**

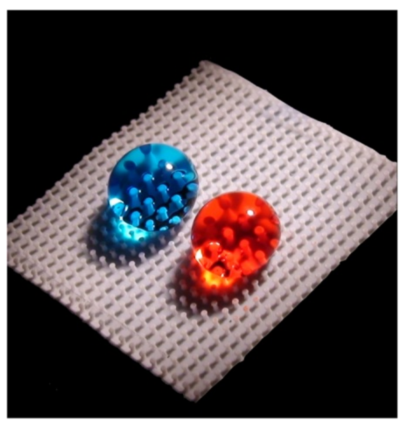



**Layered silicates**




**Linear silicates**

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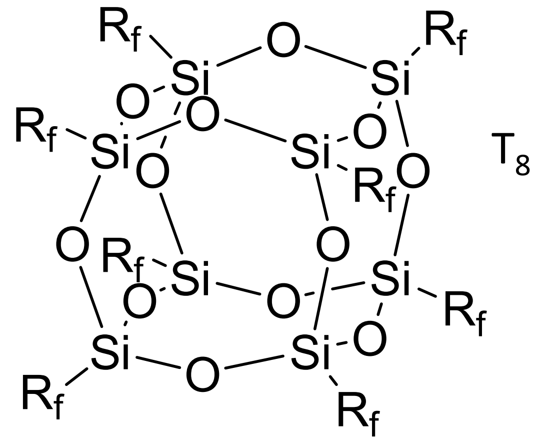
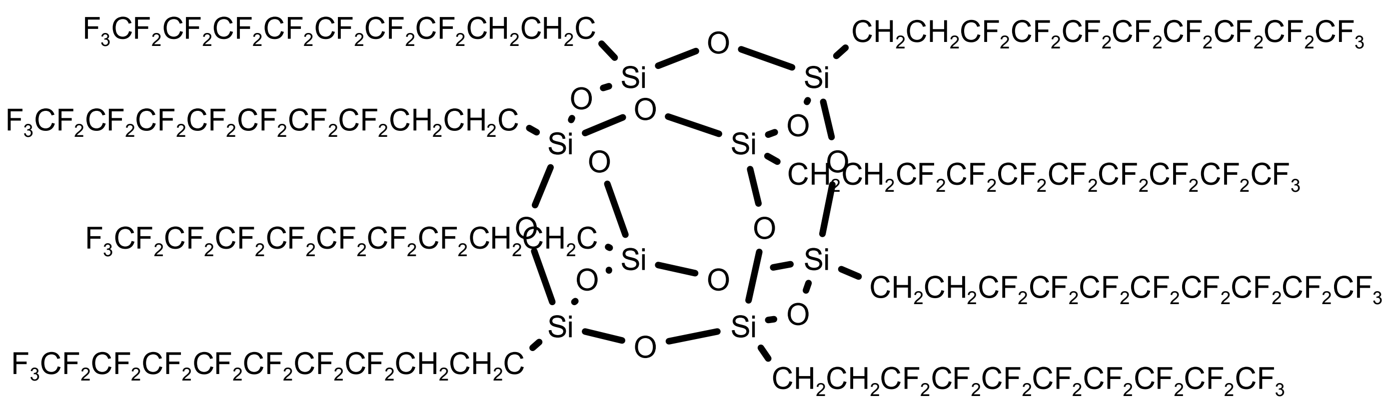
# Fluorinated POSS Synthesis

$$R_fSiX_3 \xrightarrow[\text{solvent}]{OH^-/H_2O}$$




$R_f = -CH_2CH_2(CF_2)_nCF_3$

$n = 0, 3, 5, 7$



*Angew Chem* 2008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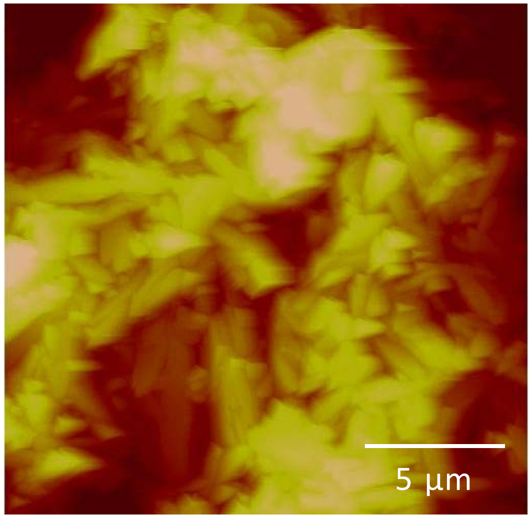
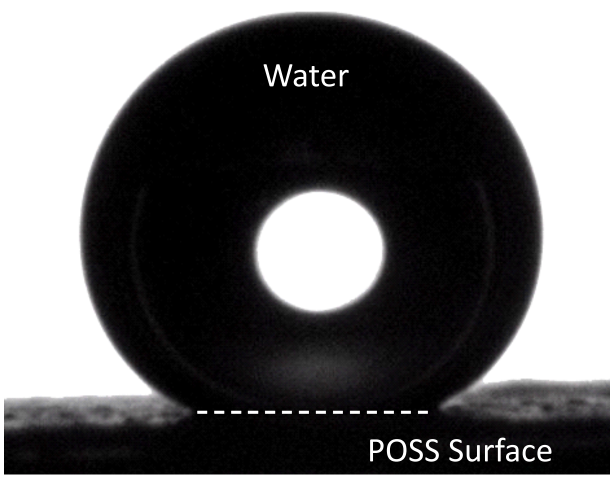
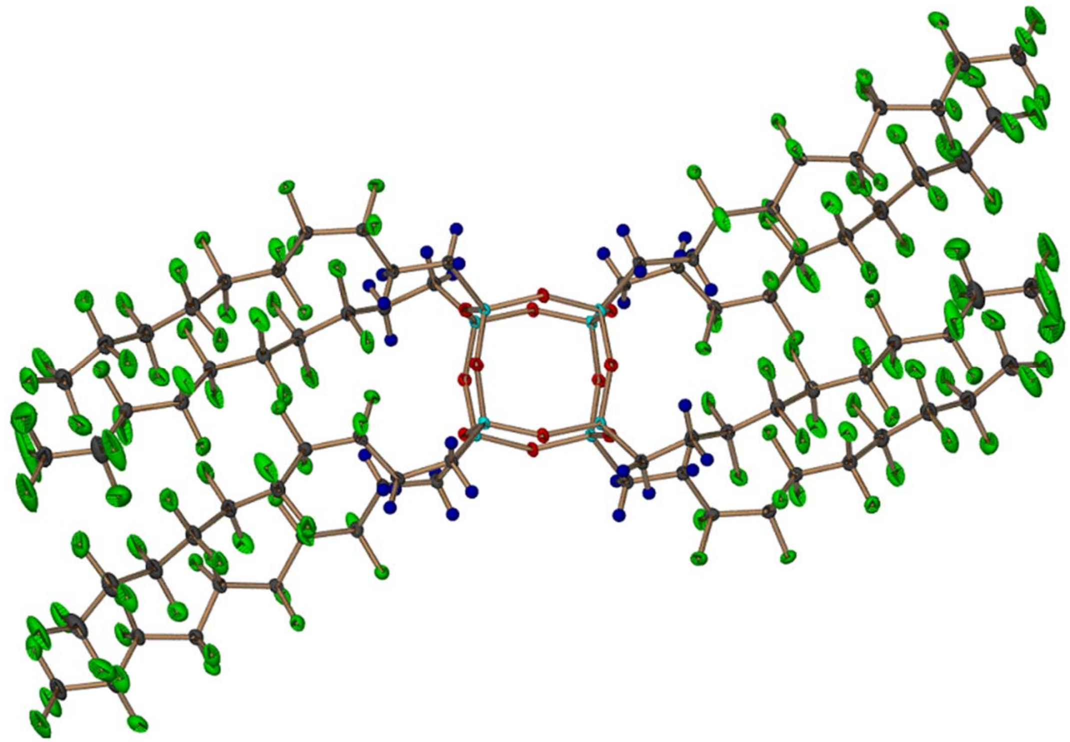
# Hydrophobic Materials




- Spin-cast surface of Fluorodecyl POSS
- ~4 µm rms roughness by AFM
- 154° Water contact angle



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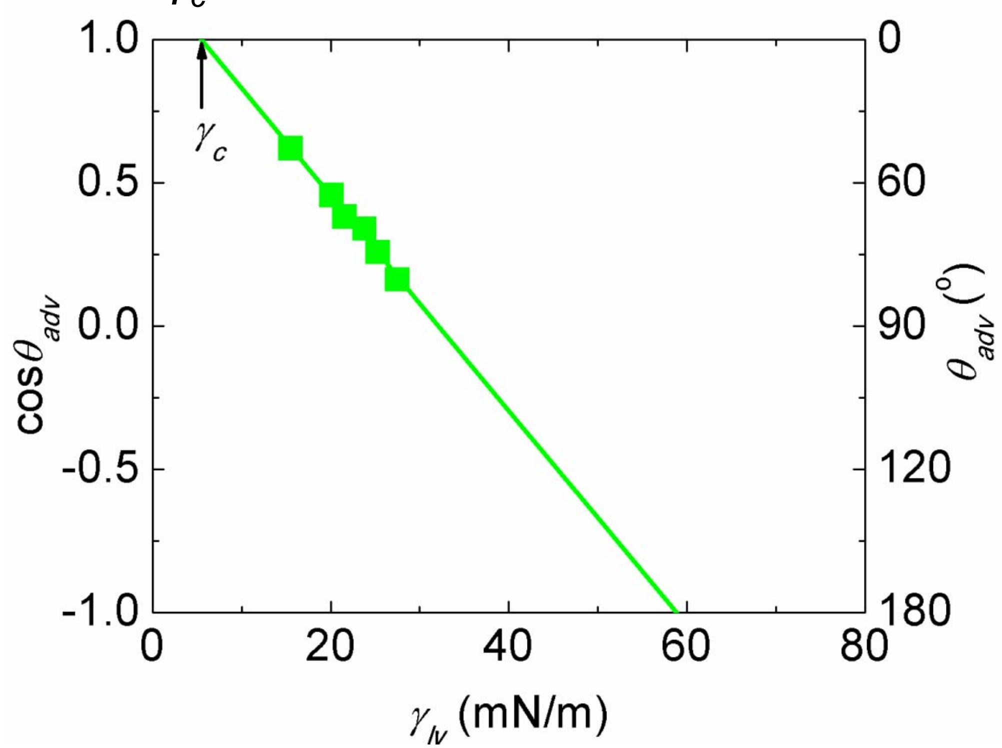
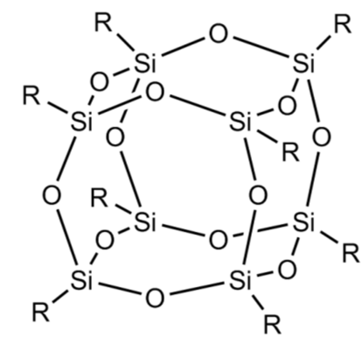
# Zisman Analysis

$\gamma_c$ = 5.5 mN/m




Fluorodecyl:
$R$ = $-CH_2-CH_2-(CF_2)_7-CF_3$

GG analysis results in surface energy calculation of: $\gamma_c$ = 8 mN/m

Contacting liquids:
hexadecane ($\gamma_{lv}$ = 27.5 mN/m), dodecane (25.3), decane (23.8), octane (21.6), heptane (20.1) and pentane (15.5)

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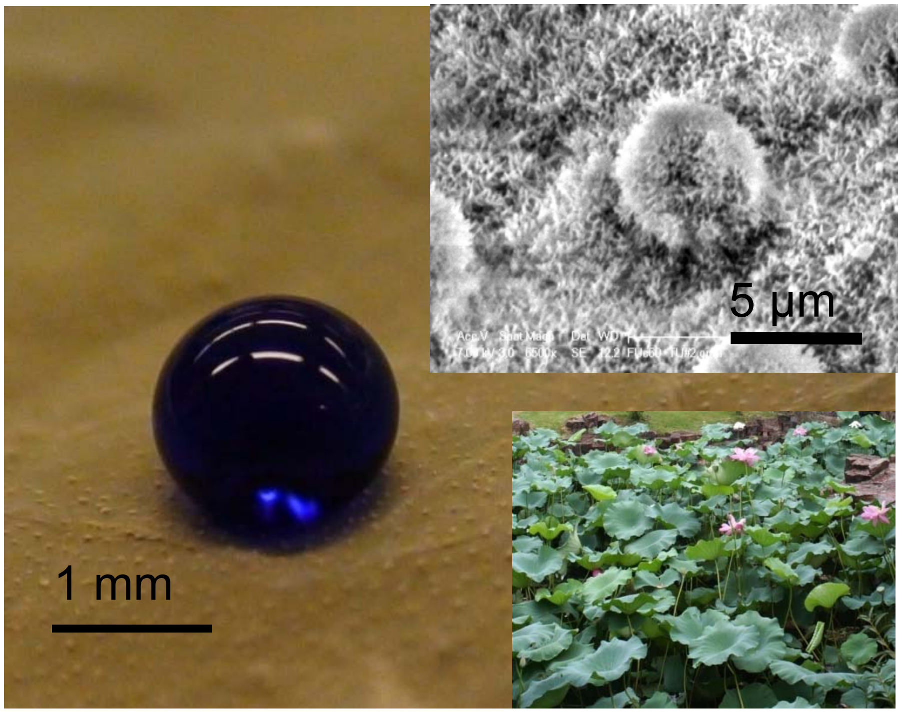
# The Lotus Leaf




Water, $\gamma_{LV}$ = 72.1 mN/m

Hexadecane, $\gamma_{LV}$ = 27.5 mN/m

On most surfaces, $\theta_{oil} < \theta_{water}$ . This is because the surface tension ($\gamma_{lv}$) of water is significantly higher than that for oils.

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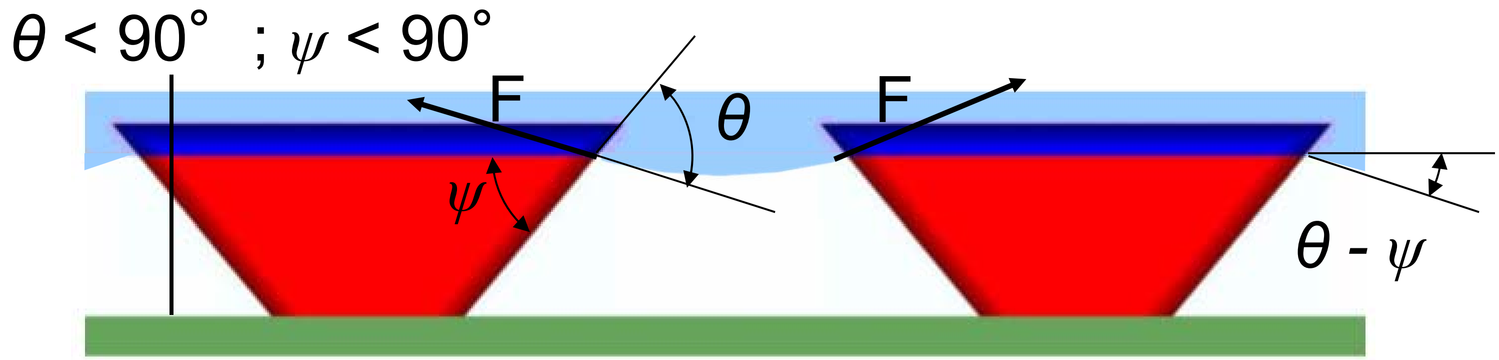
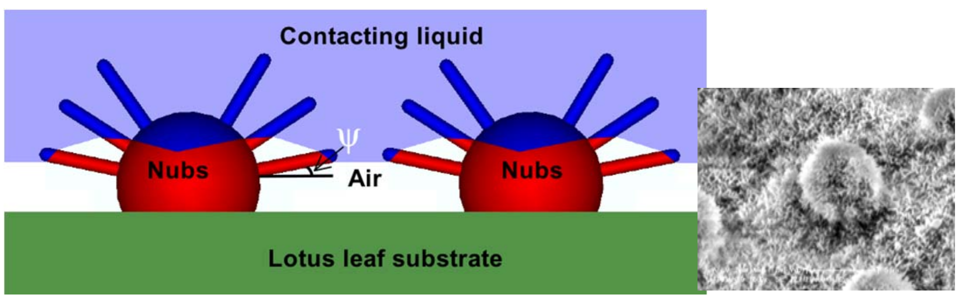
# Critical role of re-entrant texture ($\psi$ < 90°)

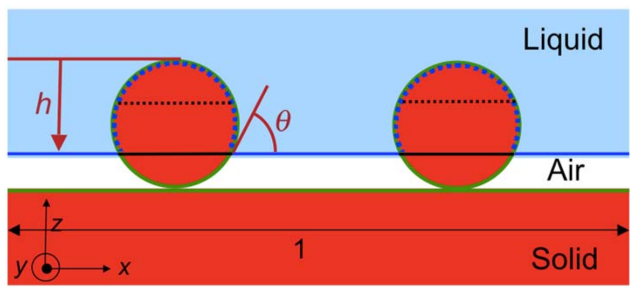



It is possible to support a composite interface even if θ < 90°

Re-entrant curvature : 180° > $\theta$ > 0°




Lotus Leaf

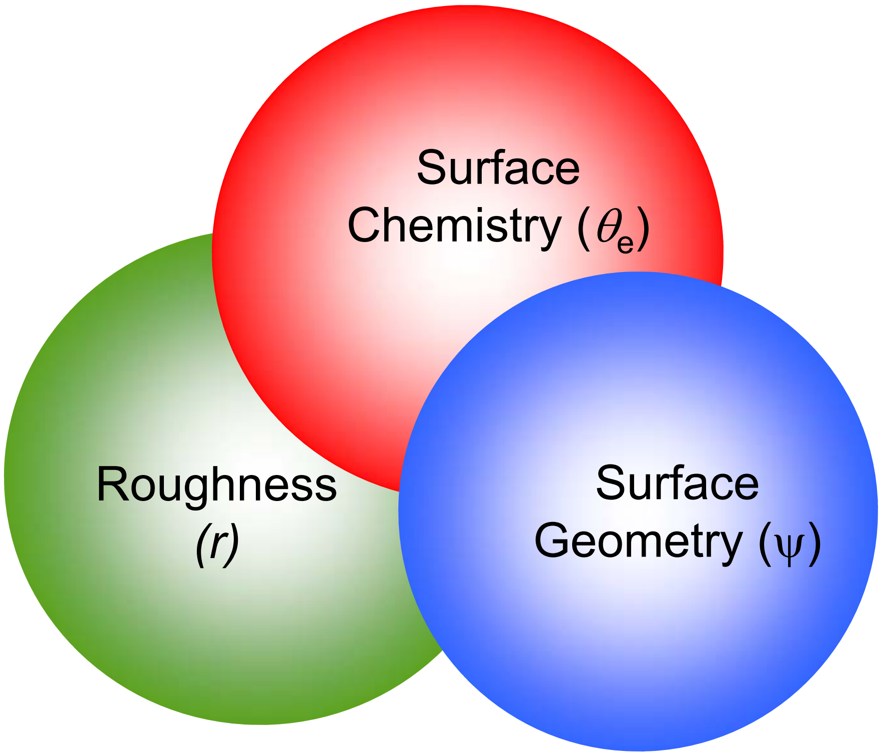



Cylinders / Fibers

Herminghaus, *Euro. Phys. Lett.* (2000), Tuteja *et al. Science (*2007*);* Tuteja et al., PNAS, (2008*).*

# Designing Omniphobic Surfaces

- **Constructing super-repellent surfaces**
  - Three key ingredients





PMMA + 44 wt% POSS
electrospun coating (beads on a string) morphology

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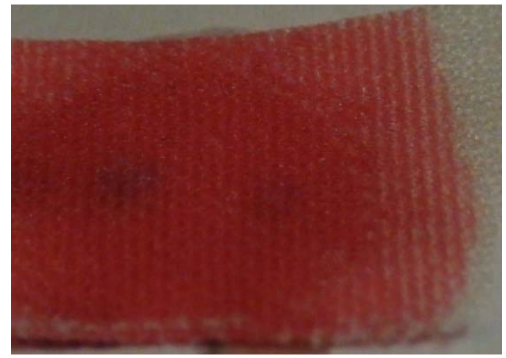
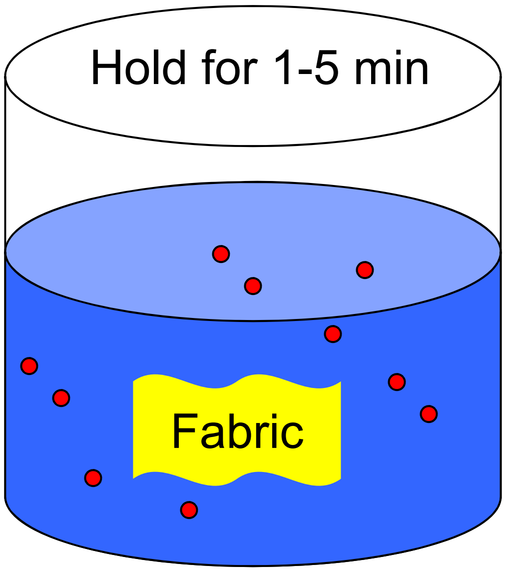
# The Dip-Coating Process

Hexadecane ($\gamma_{lv}$ = 27.5 mN/m) on an as-received commercial polyester fabric



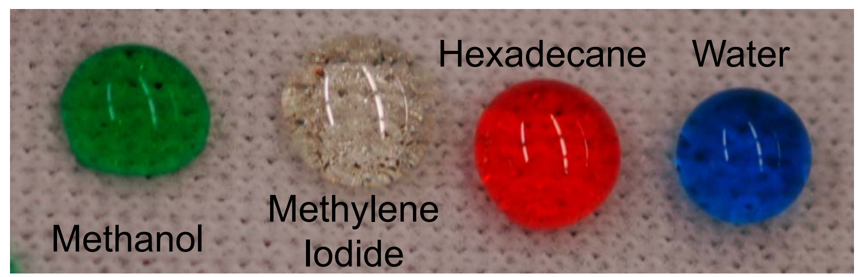
Before

Dip




Solution of fluorodecyl POSS in Asahiklin (30 mg/ml)

Dry (heat in oven at 60° C for 20 minutes)




After dip-coating with a solution of fluorodecyl POSS

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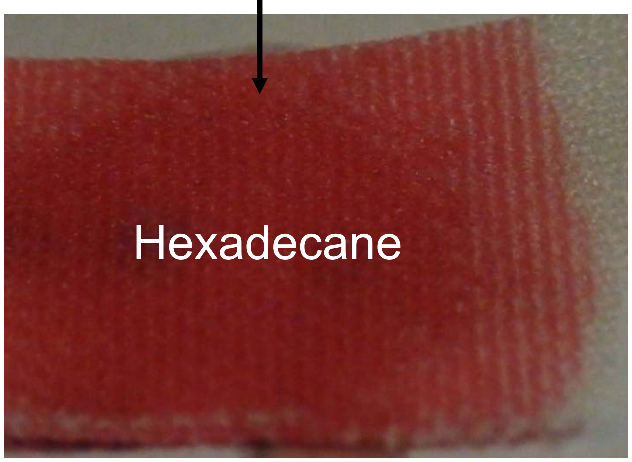
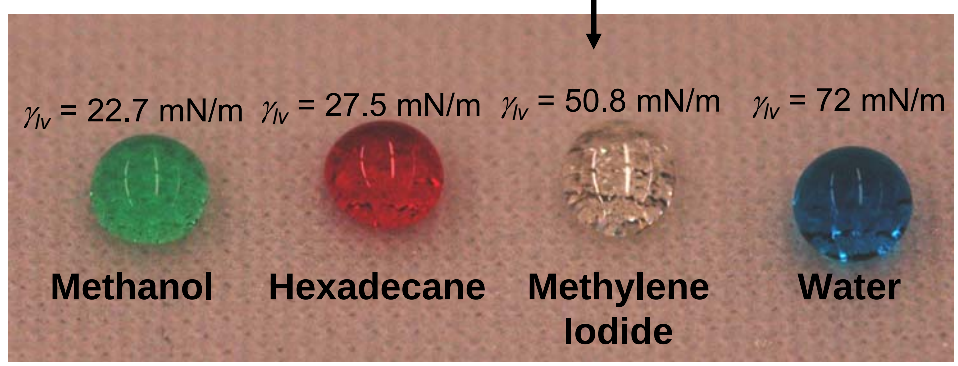
# Dip-Coated Polyester Fabric



Before coating

After coating with fluorodecyl POSS in Asahiklin (30 mg/ml)

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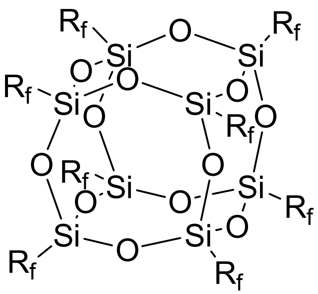
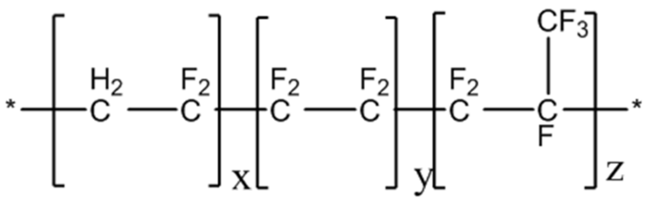
# Dip-coating process for conformal coating of textured surfaces

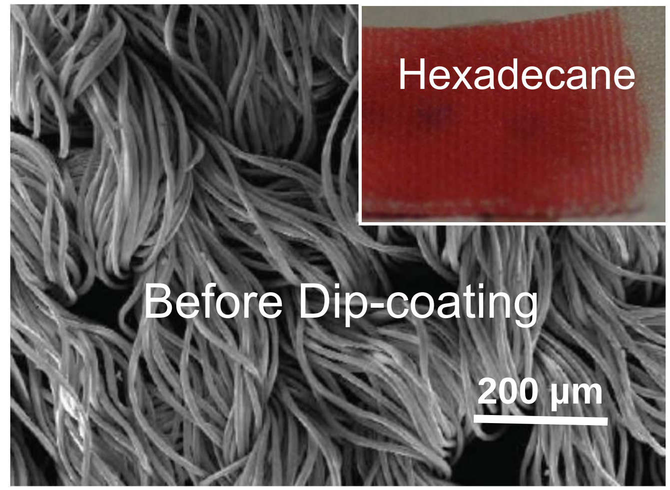


$R_f$ = $-CH_2-CH_2-(CF_2)_7-CF_3$
Fluorodecyl POSS
$\gamma_{sv} \approx 8$ mN/m



Tecnoflon® (BR9151)
Fluoro-elastomer from Solvay-Solexis
$\gamma_{sv} \approx 18$ mN/m

Anticon 100 polyester fabric




50:50 mixture, total solids = 10 mg/ml

Dip in Asahiklin solution for 5 minutes

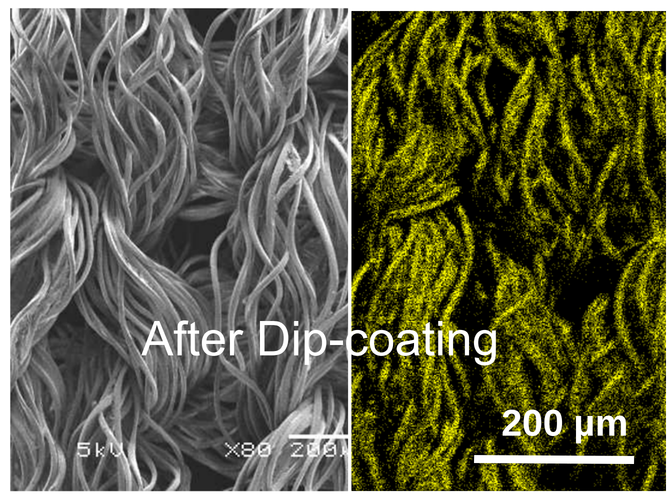
↓

Air dry to remove solvent

↓

Heat treat at 60 °C for 30 minutes

EDAXS spectrum for fluorine

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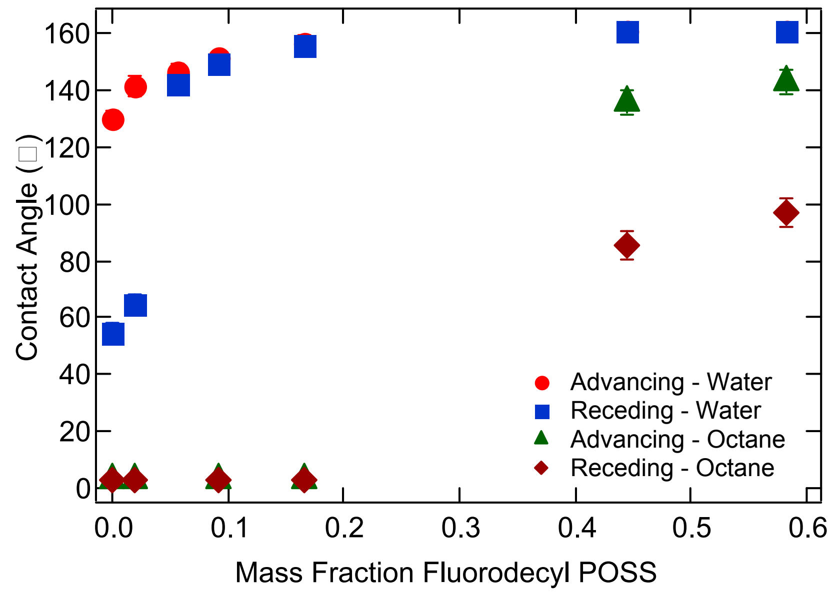
# Superhydrophobic/Superoleophilic

**Designing Superoleophobic Surfaces**

Anish Tuteja,[1] Wonjae Choi,[2] Minglin Ma,[1] Joseph M. Mabry,[3] Sarah A. Mazzella,[3] Gregory C. Rutledge,[1] Gareth H. McKinley,[2*] Robert E. Cohen[1*]

**Superhydrophobic Superoleophilic**




At low POSS concentrations many surfaces are *both* superhydrophobic and superoleophilic ($\theta^{*}_{alkane} \approx 0^{\circ}$). Thus, these porous surfaces form ideal membranes for separating mixtures / dispersions of alkanes (oils) and water

*Science*, **2007**, *318*, 1618.

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# PEGDA + Fluorodecyl POSS

Can hydrogen bond with water

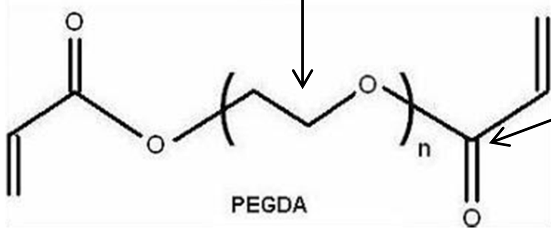
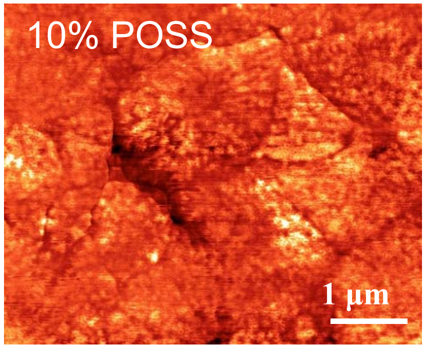
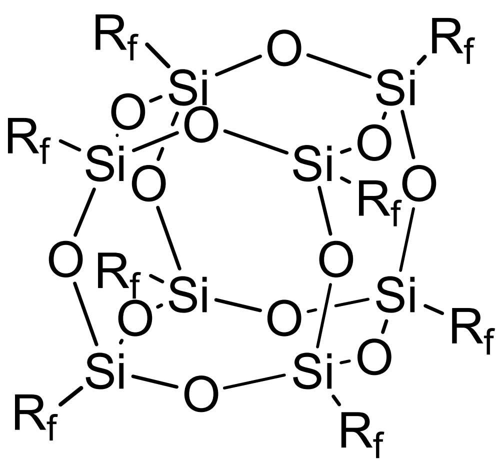



Photo-crosslinkable

AFM Phase images of spin-coated PEGDA + POSS films


Fluorodecyl POSS molecules preferentially segregate to the air interface and crystallize.

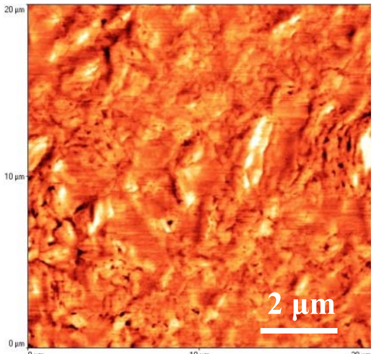


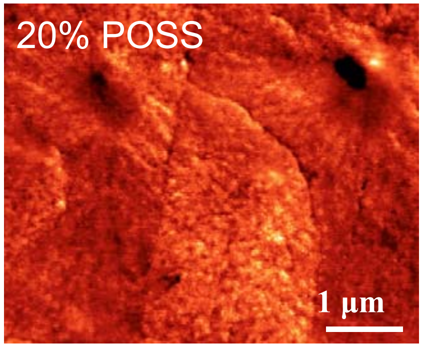

$R_f$ = $-CH_2-CH_2-(CF_2)_7-CF_3$

Fluorodecyl POSS

$\gamma_{sv} \approx 8$ mN/m

20% POSS
Under water

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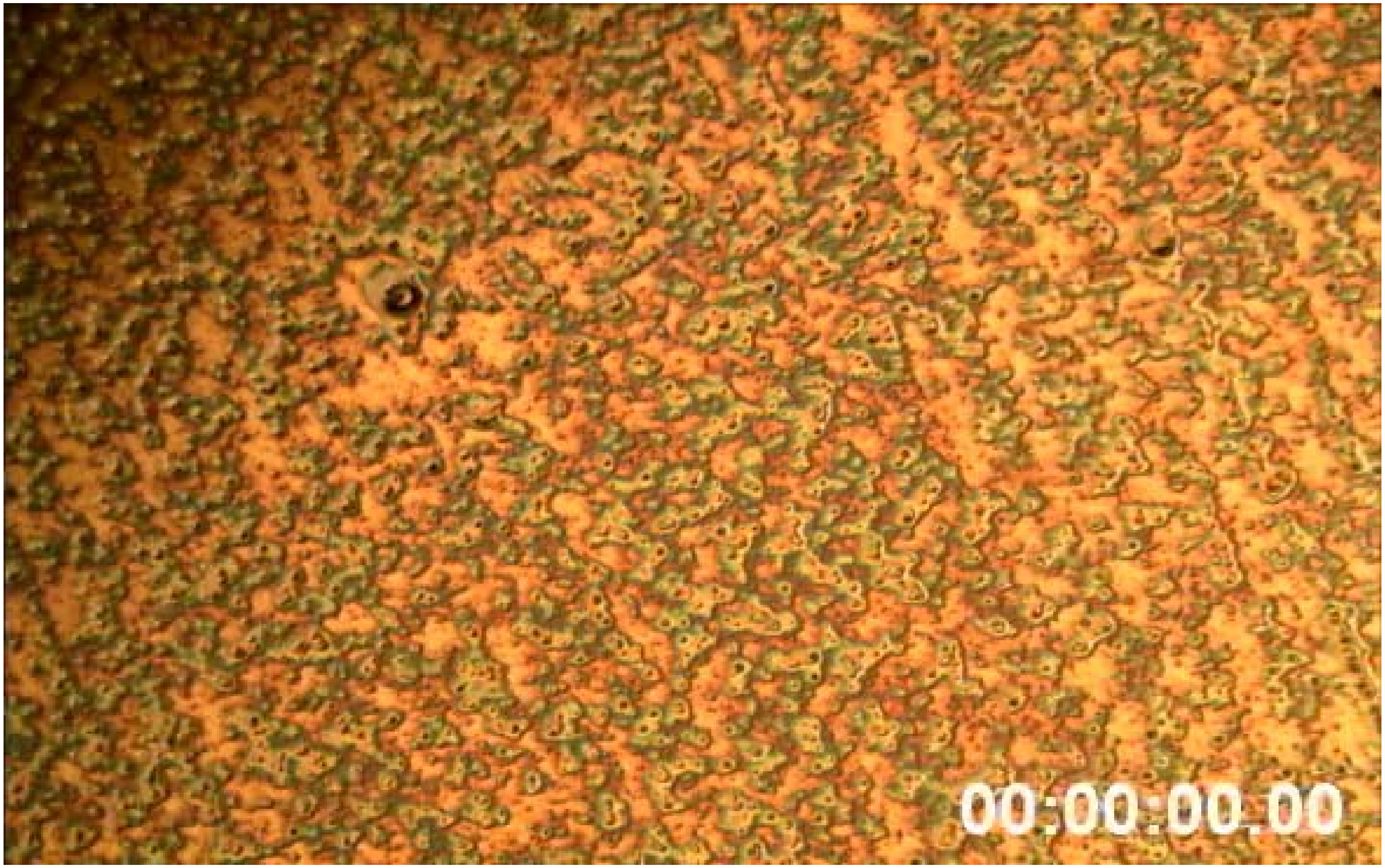
# PEGDA + Fluorodecyl POSS

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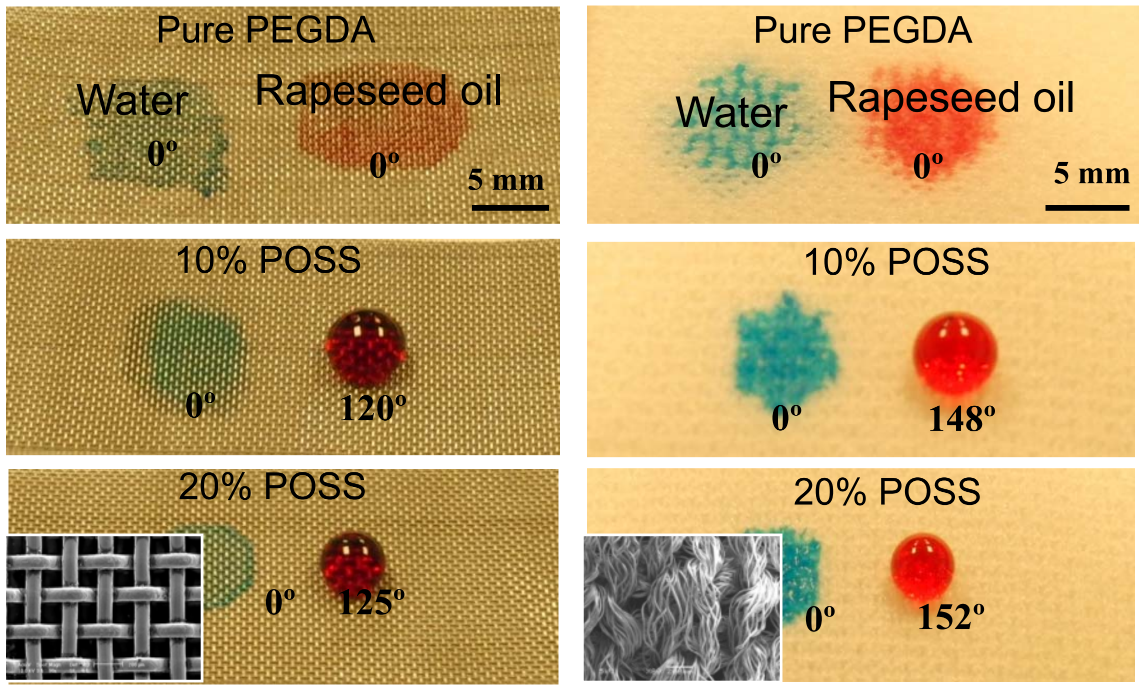
# PEGDA + fluorodecyl POSS blends

Surfaces with inherent re-entrant curvature **dip-coated** with PEGDA + POSS blends




Stainless Steel Wire Mesh     Commercial Polyester Fabric

PEGDA surface reconfiguration leads to superhydrophilic behavior.

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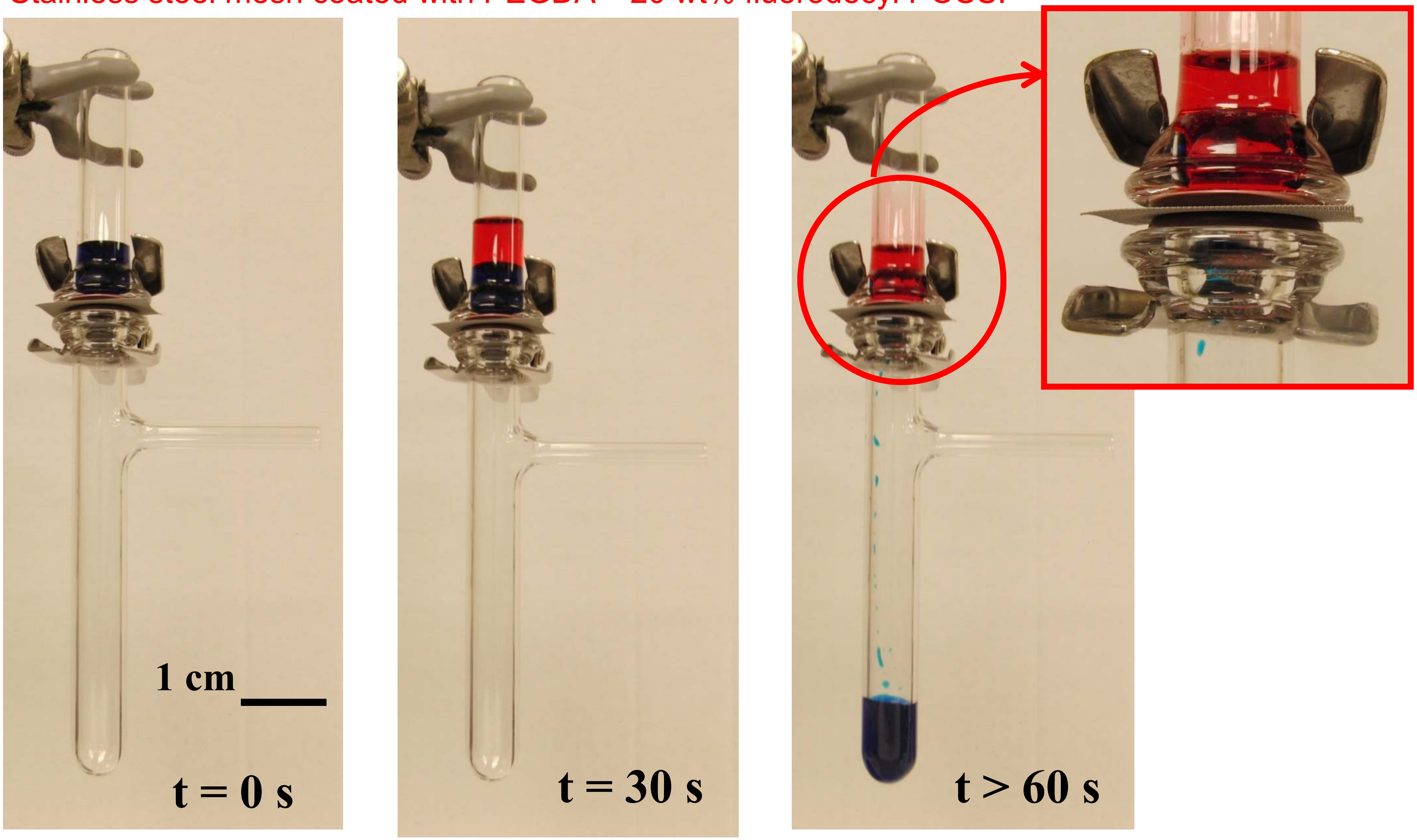
# Free oil – water separation

Stainless steel mesh coated with PEGDA + 20 wt% fluorodecyl POSS.

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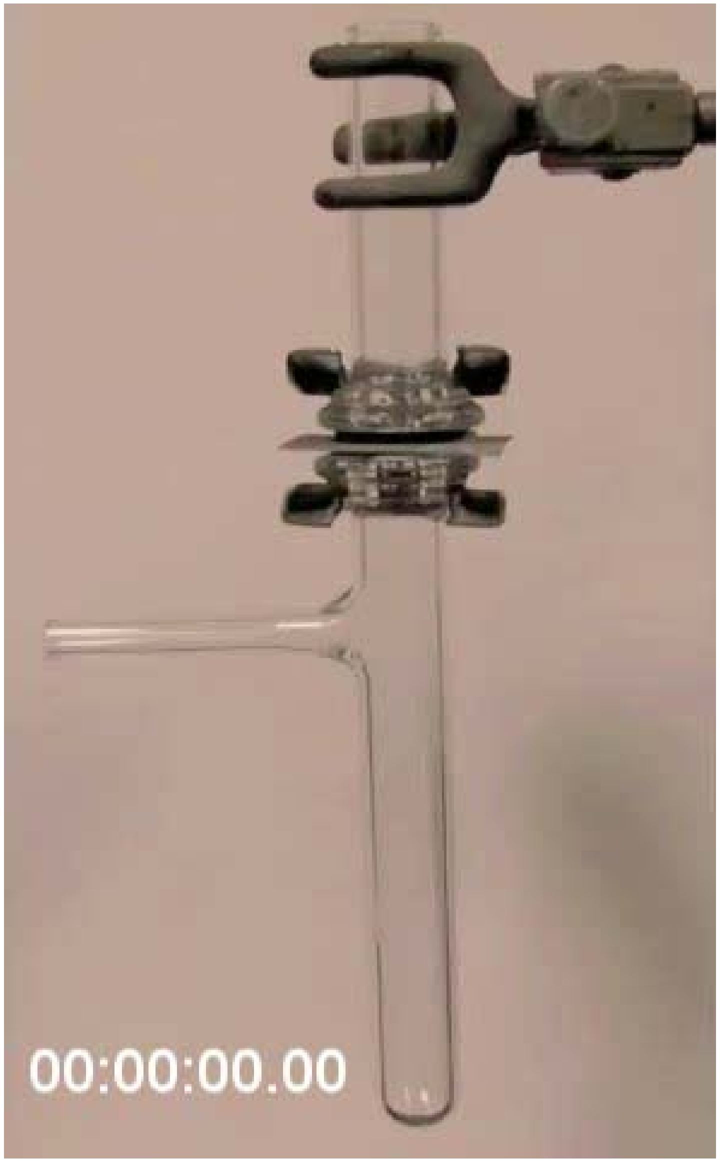
# Free oil – water separation

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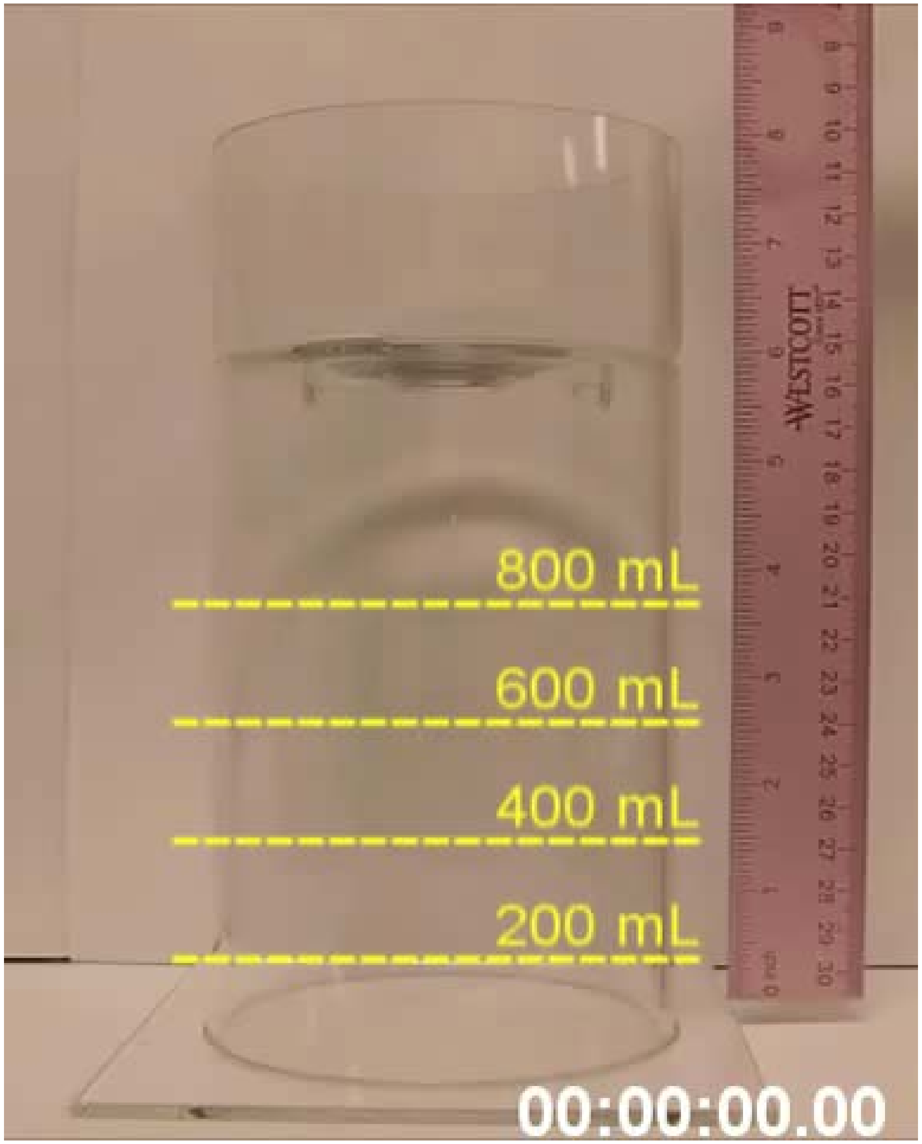
# 1-Liter scale separation

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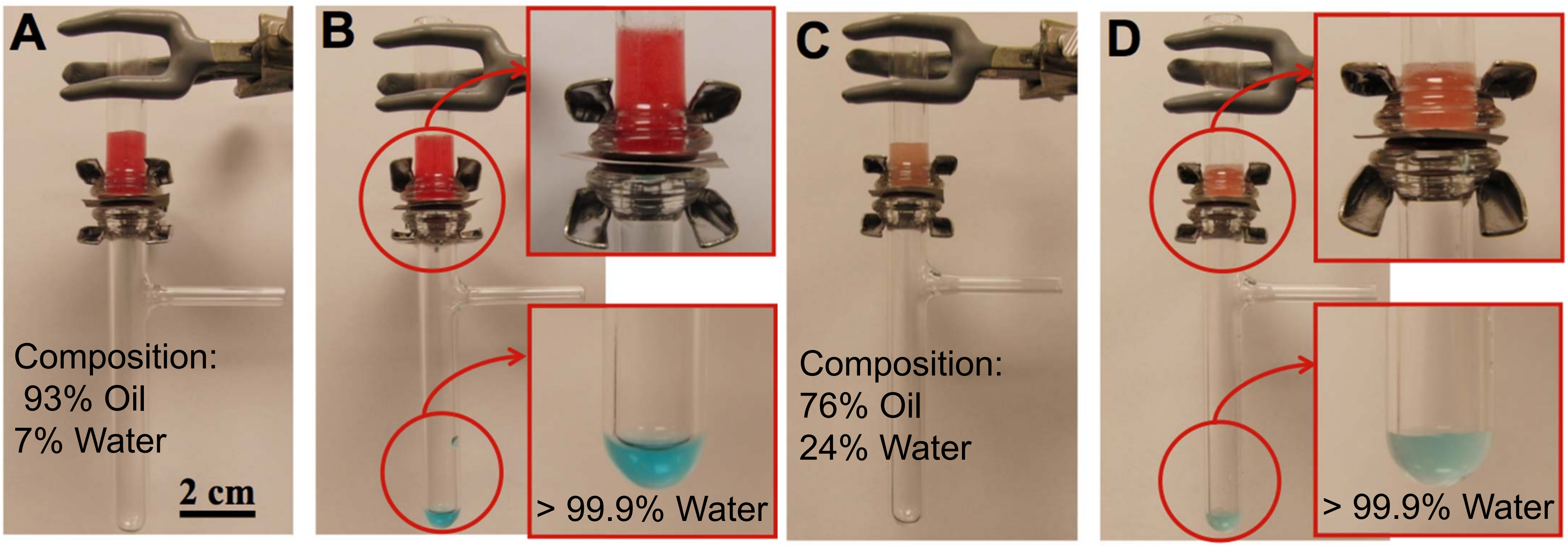
# Separation of Oil-Water Emulsions

Water-in-Oil Emulsion

Oil-in-Water Emulsion




A simple, scalable, gravity-based system for the separation of both oil-in-water and water-in-oil emulsions. This is one of the first gravity-based systems to achieve such high emulsion separation efficiencies.

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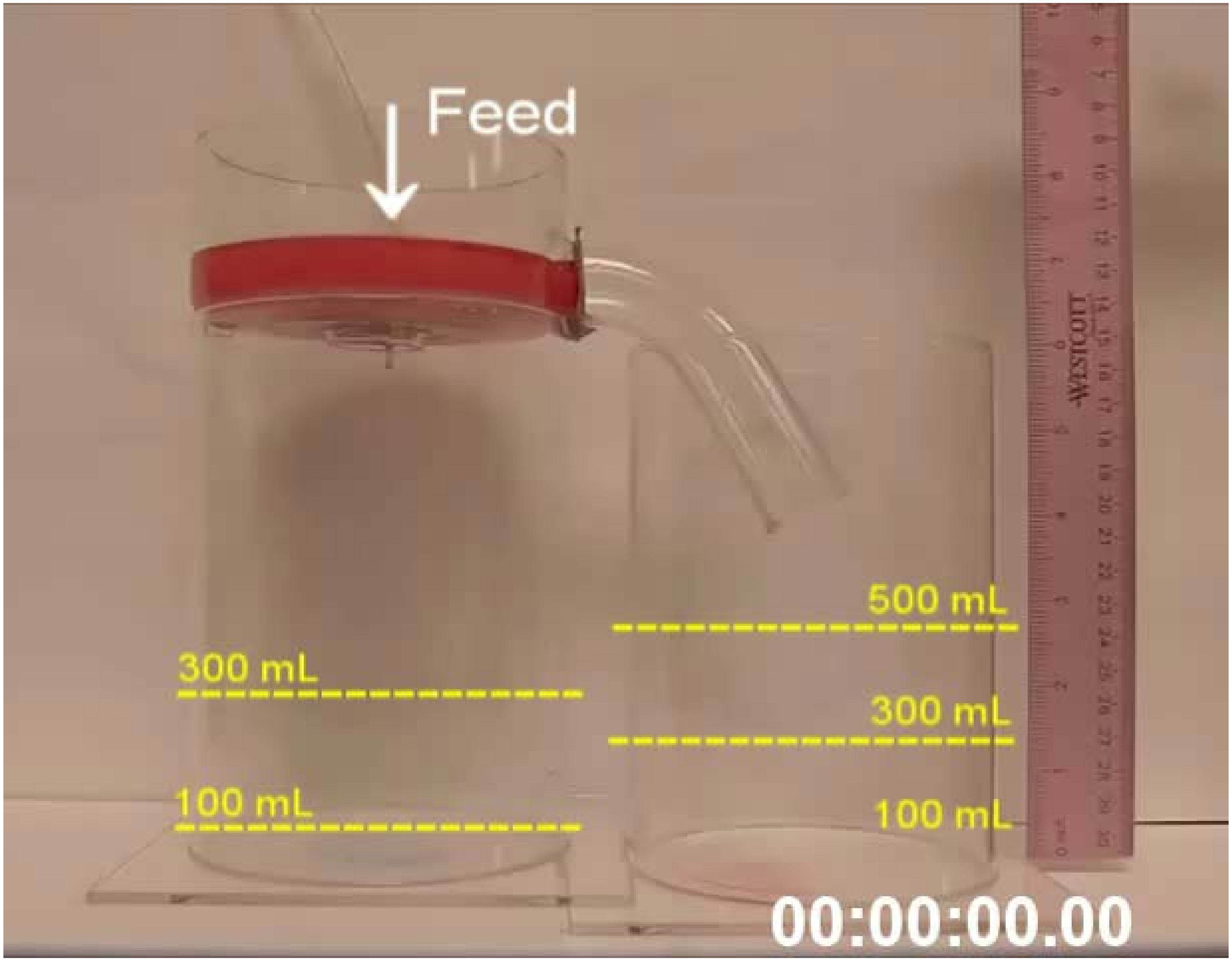
# Gravity-driven, continuous-flow device

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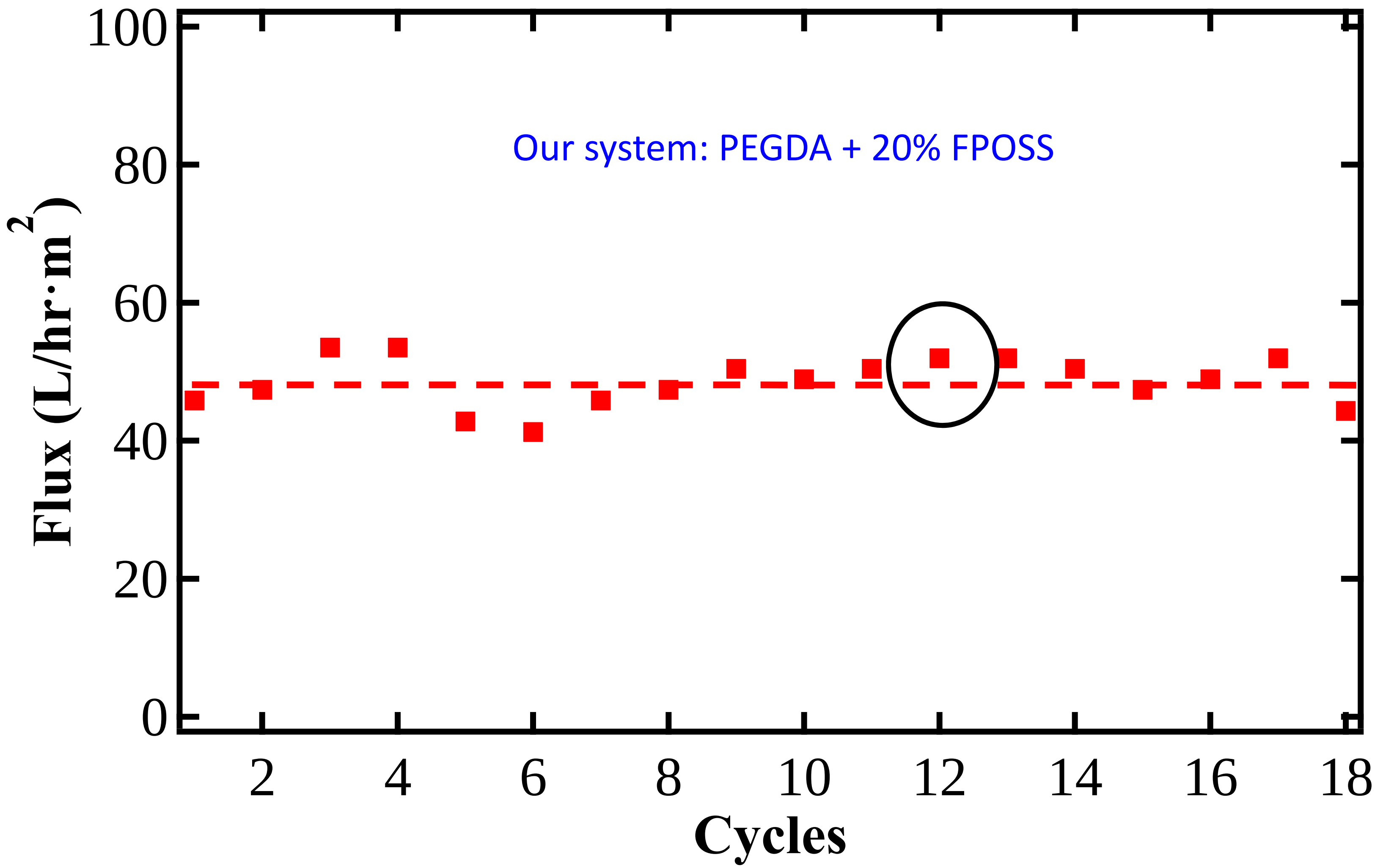
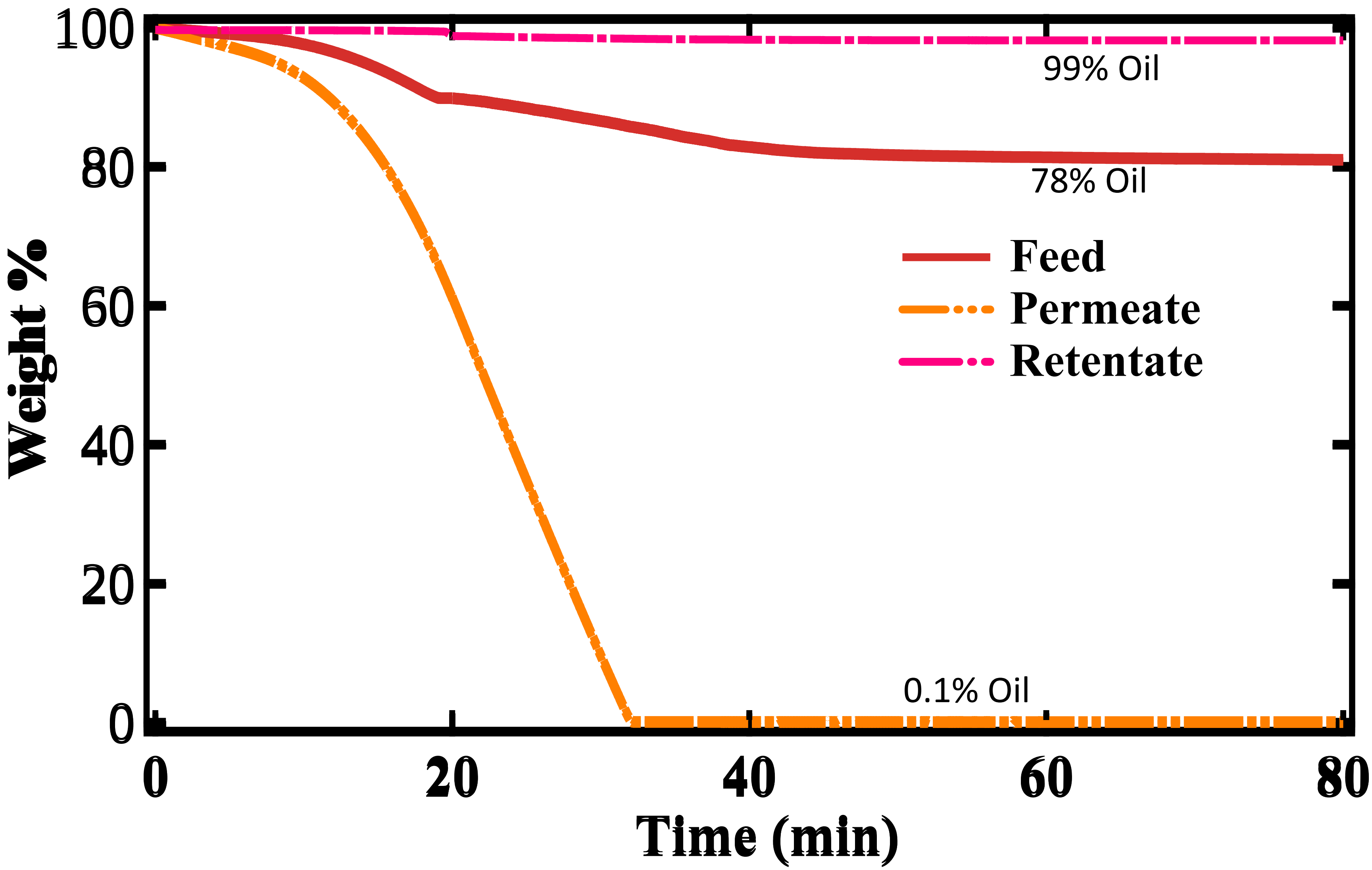
# Oil-Water Emulsion Separation



# Separation Efficiency

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# Summary

• We have developed surfaces that for the first time are superhydrophilic and superoleophobic.

• Such surfaces are ideal for the separation of both free-oil and oil-water emulsions.

• The designed membranes, for the first time, allow continuous-flow oil-water emulsion separation.

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# Acknowledgements

Professor Anish Tuteja

*Oil/Water Separation Membranes*

Polymer Working Group

*Fluorinated POSS*

## *Financial Support*

*Air Force Office of Scientific Research*

*Air Force Research Laboratory, Propulsion Directorate*

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# Impact of a Novel Fuel Processing Technique


**Payload:**
**$0.5B - 2B**
**10-15 yr.**

**Launch Vehicle:**
**$40M - 100M**

**Fuel**
**$100k**

**Availability**
- Logistics / Transportation
- Feedstock Variance

**Performance**
- Reusability / Durability
- Composition Optimization

**Raw Material Cost**
- Refining Process
- Fluctuations in fuel source and economy

**Fuel Cost**

**Price of fuel is influenced by many variables other than raw material cost**

**A novel fuel processing technique will enable:**
**Composition modification without the need of large refineries**
**Preparation of fuel in remote locations**
**Assured access**
**Reduced logistics costs**

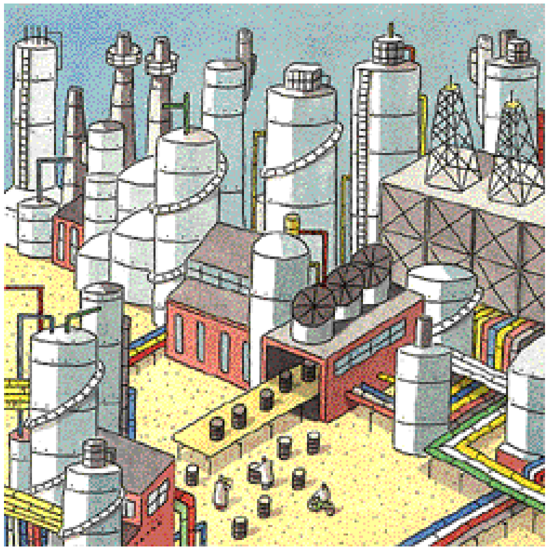
**Removal of Aromatics**
- Udex
- Sulfolane
- Lurgi Arosolvan

**Sulfur Removal**
- Hydrodesulfurization

Dye removal

Novel Liquid-Liquid Extraction Process

# Vision



**To develop the capability to produce high-performance military fuels at reduced cost with increased availability.**

# Thesis: Use $\ell/\ell$ extraction to provide improvements in several critical areas

- Reduced supply-chain logistics
- Decreased risk of supply interruption

**Availability**

- Reduced coking
- $I_{sp}$ improvement
- Improved thermal stability

**Performance**

- Reduced logistics cost
- Less Expensive feed streams

**Cost**

**Objective:** Utilize liquid/liquid extraction process to improve performance, increase availability, and reduce cost of RP by producing these fuels from less expensive feed streams.

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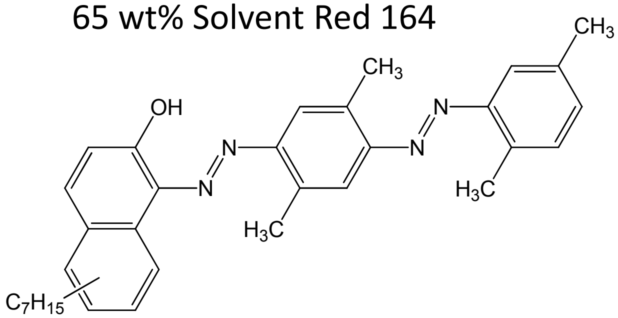
# Undesirables in RP-1

**Oil Red B4 (ORB4)**

Dye in RP-1

65 wt% Solvent Red 164




15-30 wt% xylene

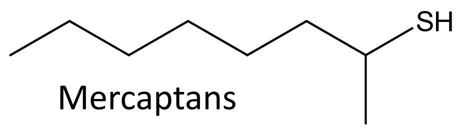
5-10 wt% ethylbenzene

**Detrimental to Thermal Stability!**

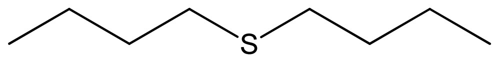
**Sulfur Compounds**

Present in RP-1

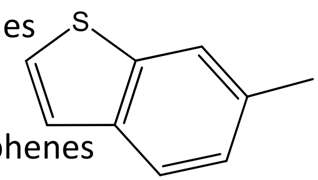
Concentration varies




Mercaptans




Sulfides



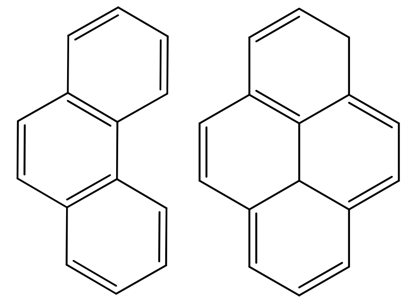

Thiophenes

**Catalysts for Coking Reactions**

**Aromatics**

Present in RP-1

Concentration varies



**Detrimental to Performance**

**RP-2 is expensive and requires an additional supply chain, which also consumes resources and may be put at risk due to unforeseen circumstances.**

**Removal from less expensive feed streams will increase availability, reduce supply risk, reduce cost, and improve performance.**

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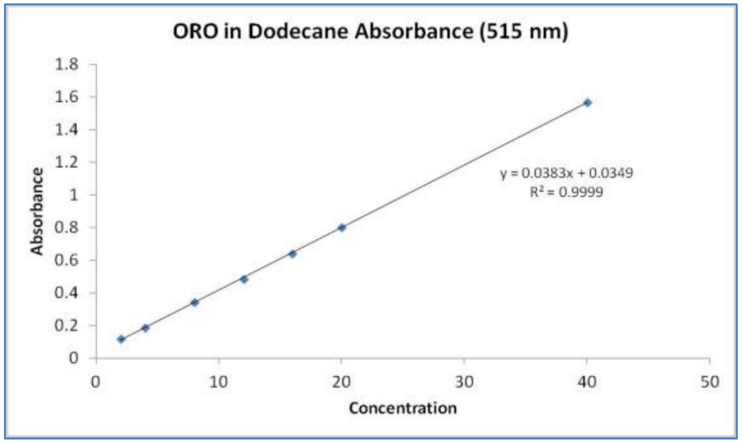
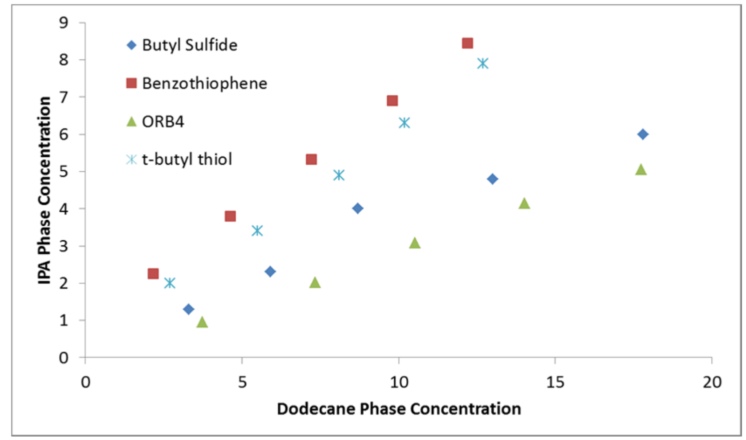
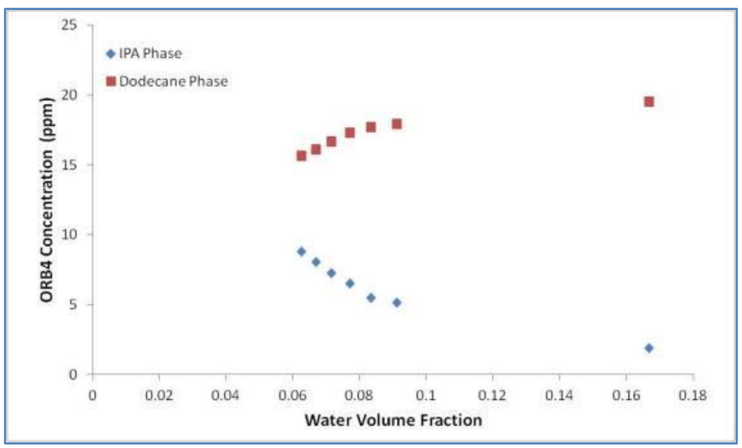
# Extraction Parameter Determination



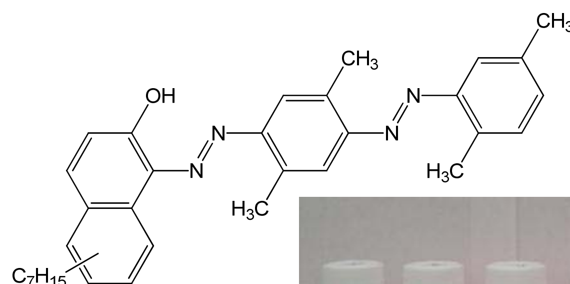

**Visible spectroscopy was used to determine concentration of dye from 2-40 ppm.**




**Small scale extractions show IPA is the most efficient extraction solvent for dyes.**




**Higher IPA : Water ratio results in higher dye concentration.**




**Optimum IPA : Water ratio is ~13 : 1 based on small scale extractions.**

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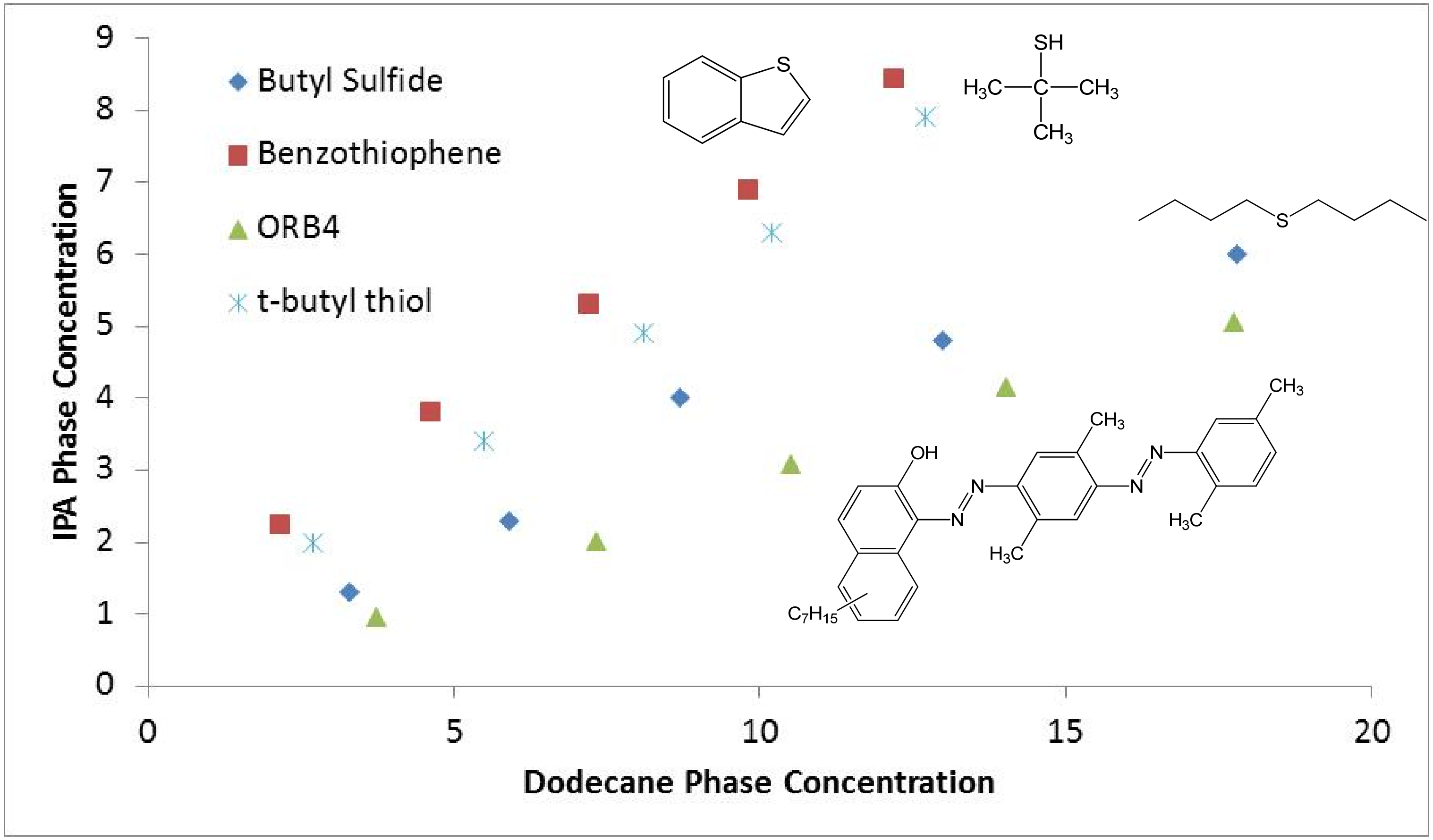
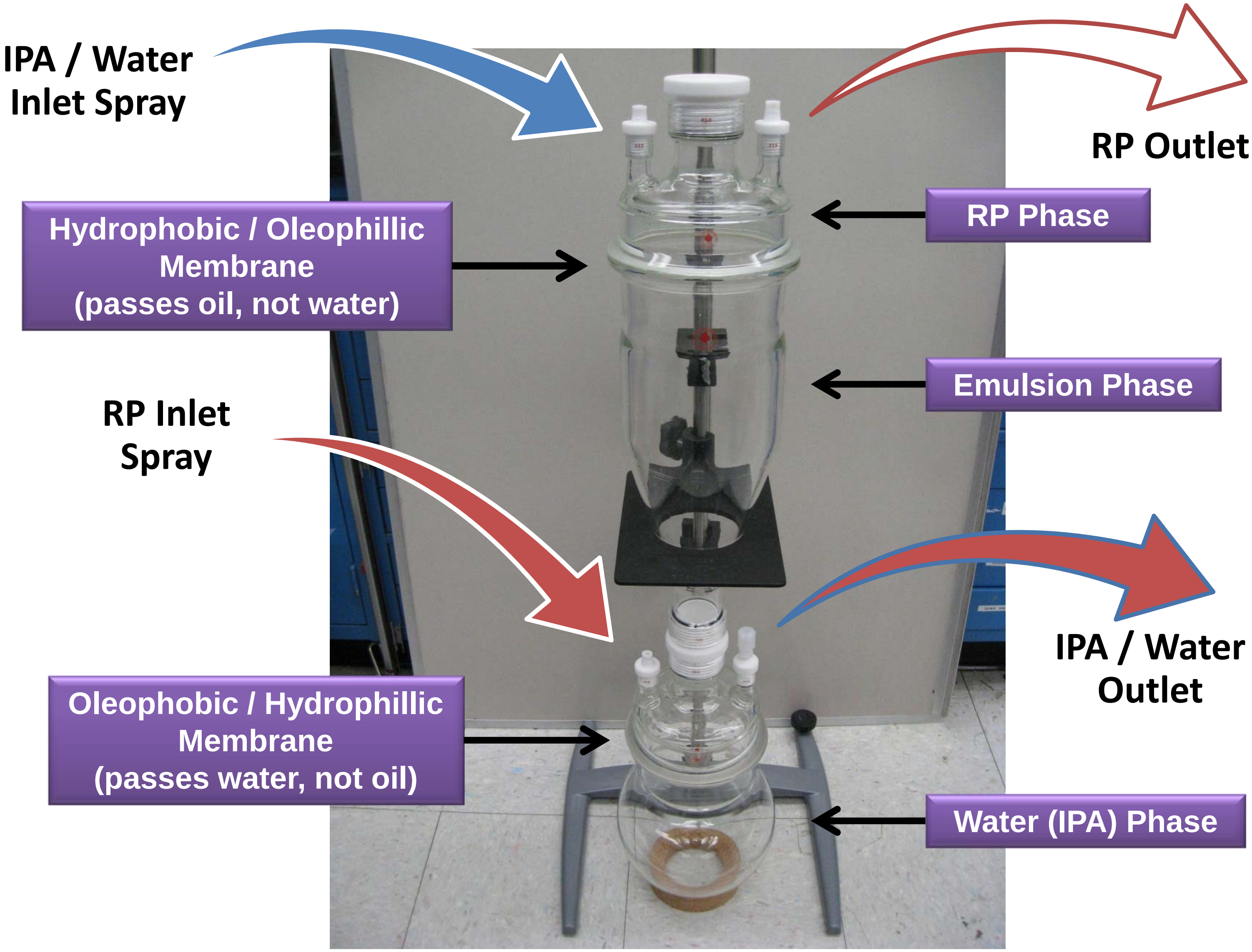
# Extraction Curves




**Equlibrium curve for compounds extracted from dodecane with IPA:water 10:1 v:v ratio**

# Extraction Apparatus

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# Extraction of Sulfur from RP-1

| Sulfur Compounds by GC-SCD (Sulfur Speciation) | Concentration (ppm) |
|---|---|
| C2 Thiophenes | <0.1 |
| C3-C4 Thiophenes | 1.6 |
| C5 Thiophenes | 6.3 |
| C6 Thiophenes | 6.1 |
| C7 Thiophenes | 5.8 |
| C8-C9 Thiophenes | 4.9 |
| C10 Thiophenes | 1.3 |
| C11 Thiophenes | 0.9 |
| C12+ Thiophenes | 2.0 |

**Standard Grade RP-1**
(Errors are ±0.3 ppm**)**

| Sulfur Compounds by GC-SCD (Sulfur Speciation) | Concentration (ppm) |
|---|---|
| C2 Thiophenes | 0.3 |
| C3-C4 Thiophenes | 1.4 |
| C5 Thiophenes | 3.7 |
| C6 Thiophenes | 3.5 |
| C7 Thiophenes | 4.1 |
| C8-C9 Thiophenes | 2.9 |
| C10 Thiophenes | 0.6 |
| C11 Thiophenes | 0.6 |
| C12+ Thiophenes | <0.1 |

**Standard Grade RP-1 after extraction with 10:1 IPA water in extraction apparatus**

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# Applied Materials Group

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QUESTIONS?
U.S. AIR FORCE