Sulfolane and Amine Mixing Behaviour in Groundwater: Implications for Pollutant Transport

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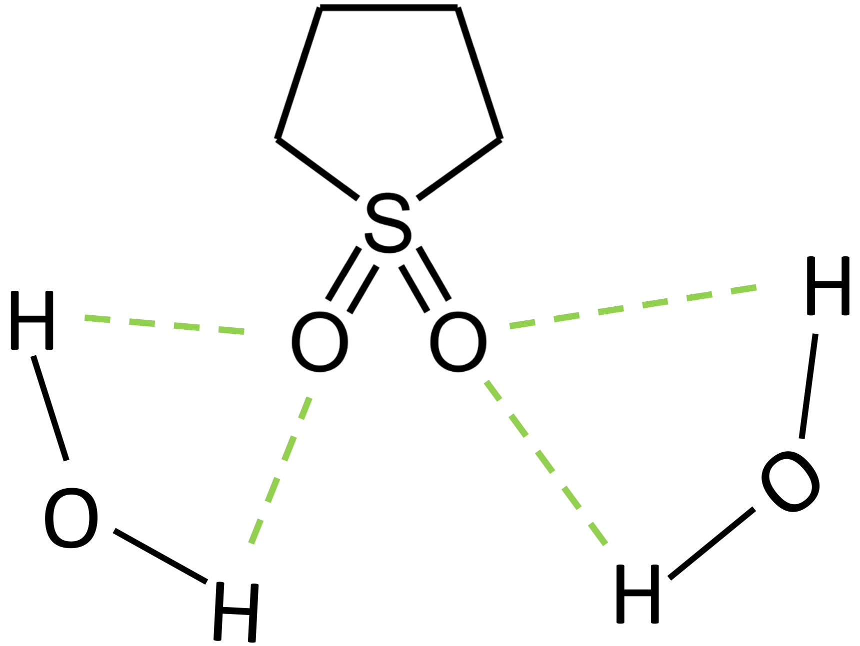
COLLEGE of ENGINEERING AND PHYSICAL SCIENCES

What is sulfolane?

- Sulfolane is used to sweeten sour gas and as a phase splitter in carbon capture and storage
- Sulfolane hampers fertility – studies are ongoing to assess toxicity
- Sulfolane plumes exist across the globe
- Sulfolane biodegrades only under aerobic conditions, and it is reported to be highly mobile due to its solubility in water, but…is this always the case?

Sulfolane Miscibility in Water

- The miscibility of sulfolane in water is due to hydrogen (H) bonding between the oxygen of the -S=O groups and the hydrogens of water

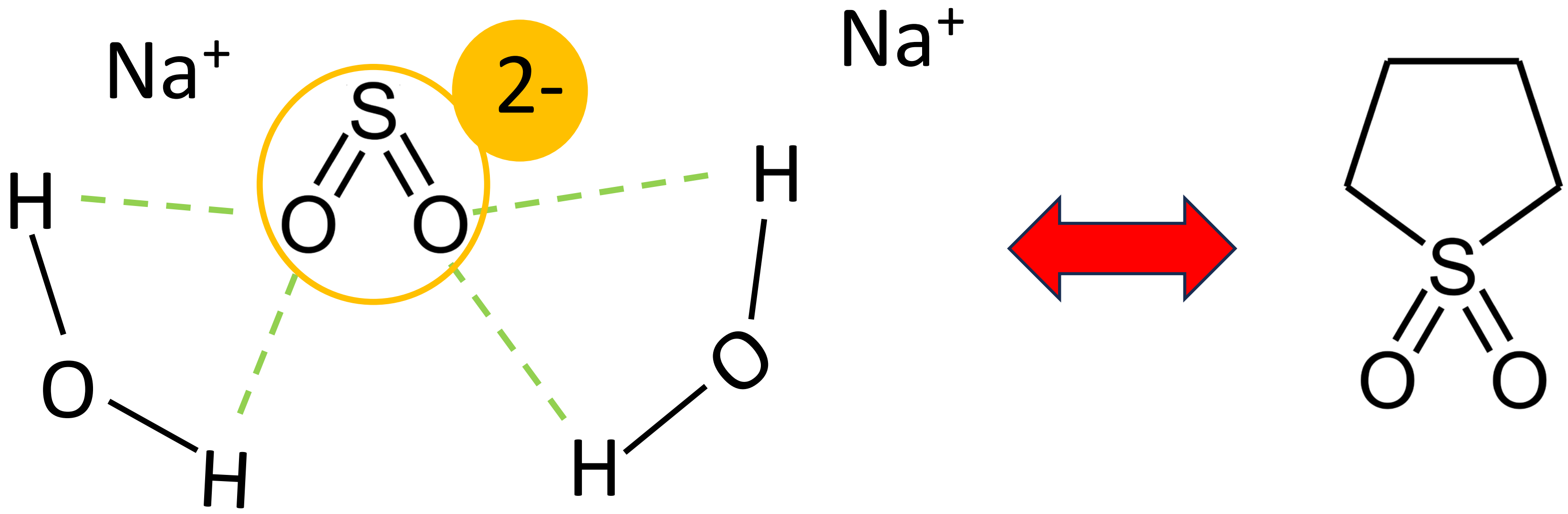


Sulfolane Miscibility in Water

- The miscibility of sulfolane in water is affected by groundwater chemistry:
  - **IONS**: naturally present or due to industrial activities, e.g., sulfate ions released from leaching of S piles
  - **Bacterial activity**: amino acid and proteins, more abundant if contaminant-degrading bacteria proliferate
  - **Co-contaminants, such as amines and hydrocarbons**

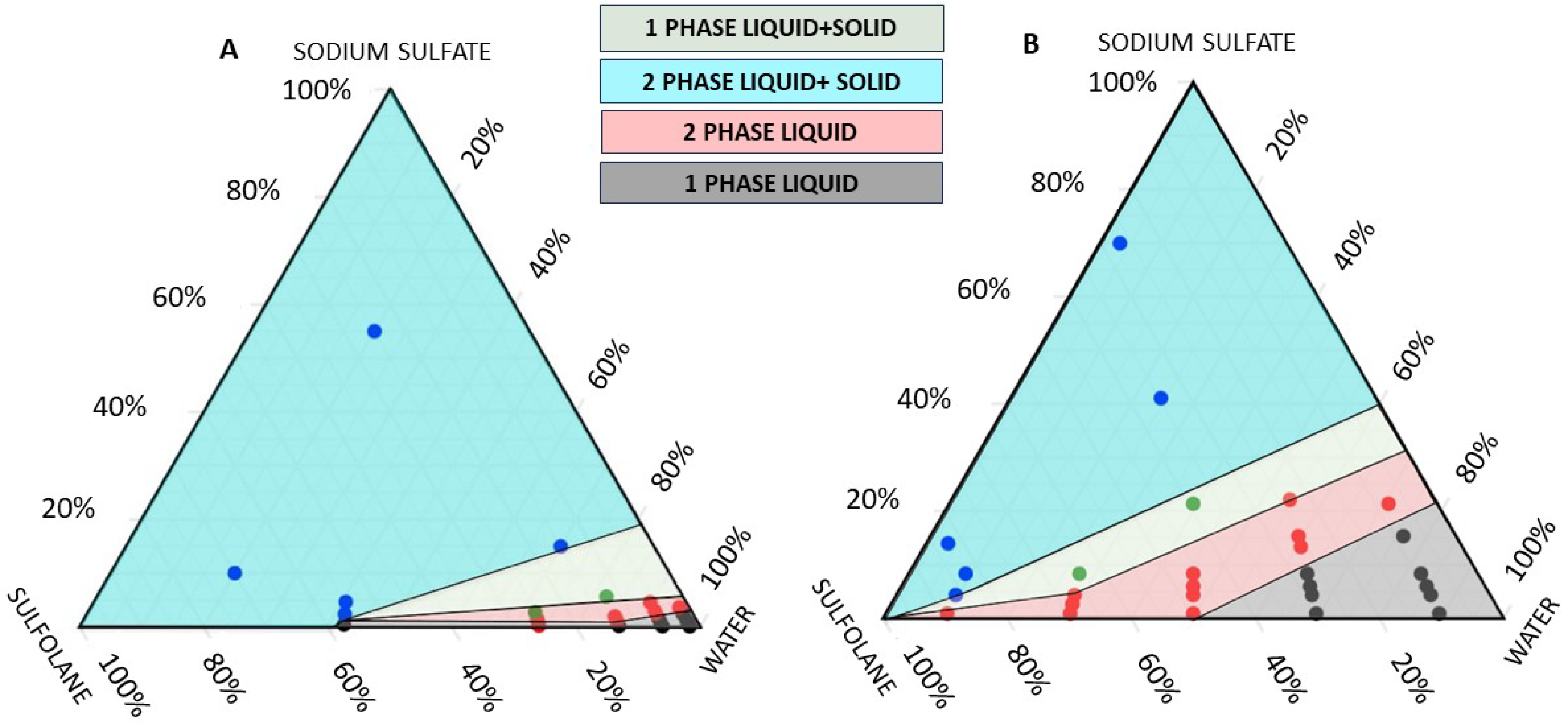
Sulfolane Miscibility in Water: Effect of Ions

- Sulfate ions in groundwater directly compete with sulfolane for H bonding with water, decreasing its miscibility
- Chloride salts have a less marked effect
- NaOH also decreases sulfolane miscibility in water



Bartokova, B., Marangoni, A.G., Laredo, T. and Pensini, E., 2023. Phase behavior of sulfolane: Potential implications for transport in groundwater. *Colloids and Surfaces A*, *677*, p.132451.

Sulfolane Miscibility in Water



MOLE PERCENT

WEIGHT PERCENT

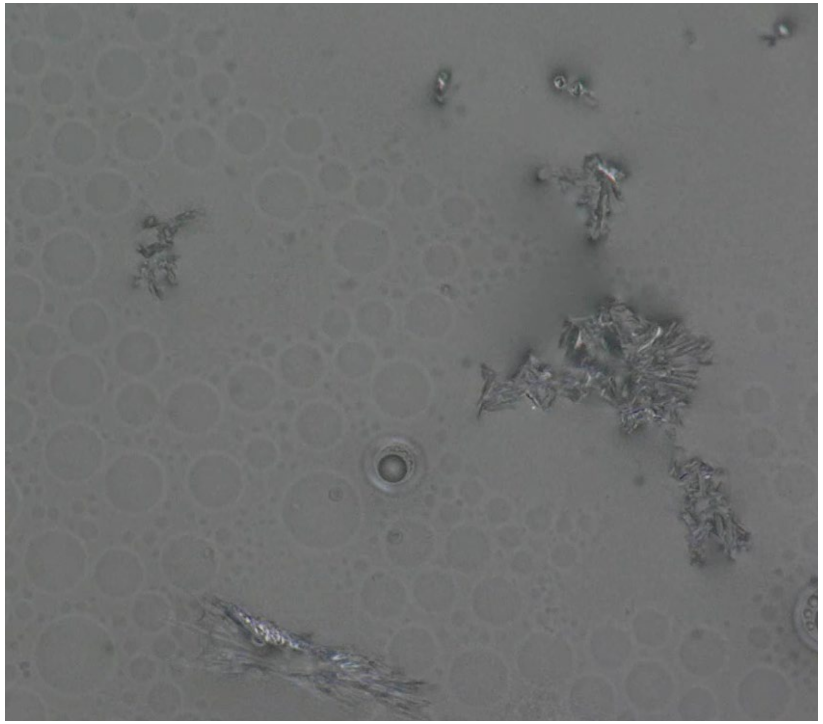
*Based on bulk separation and optical microscopy

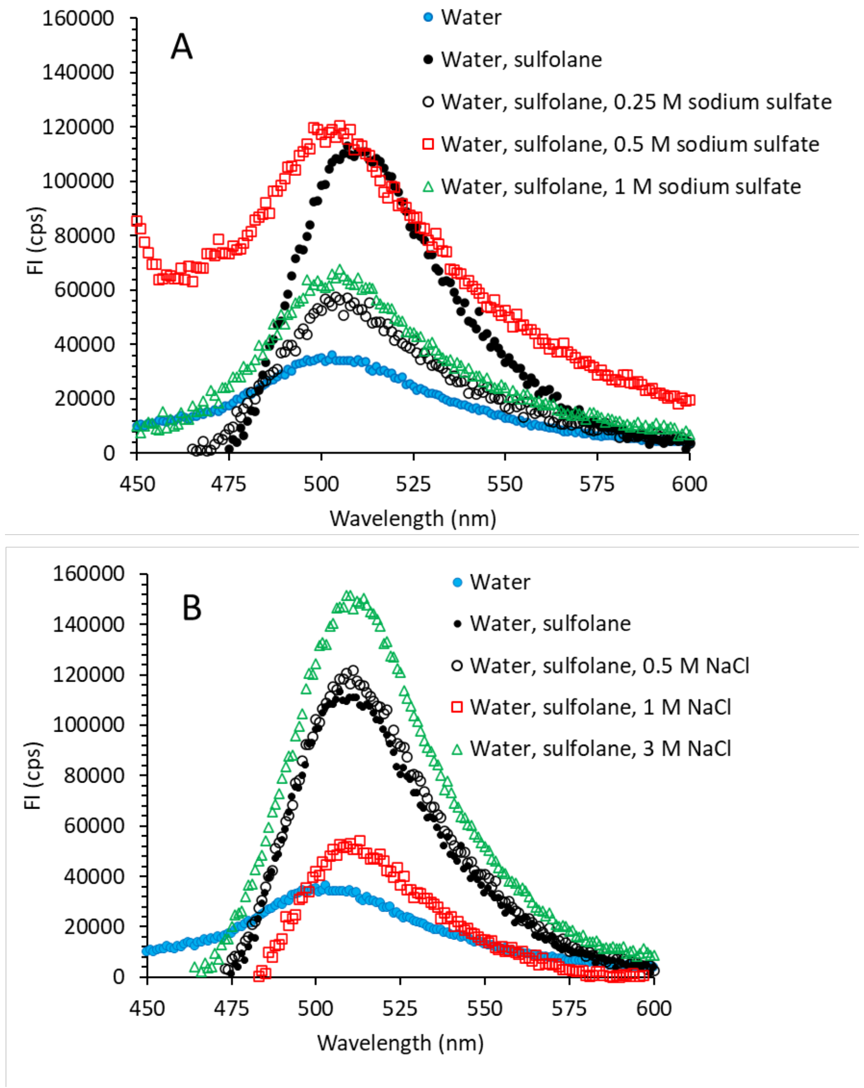
Sulfolane Miscibility in Water

- Depending on the concentration of sulfolane and sulfate salts, we observe **bulk separation, emulsification** into micron-sized droplets or **molecular clusters**

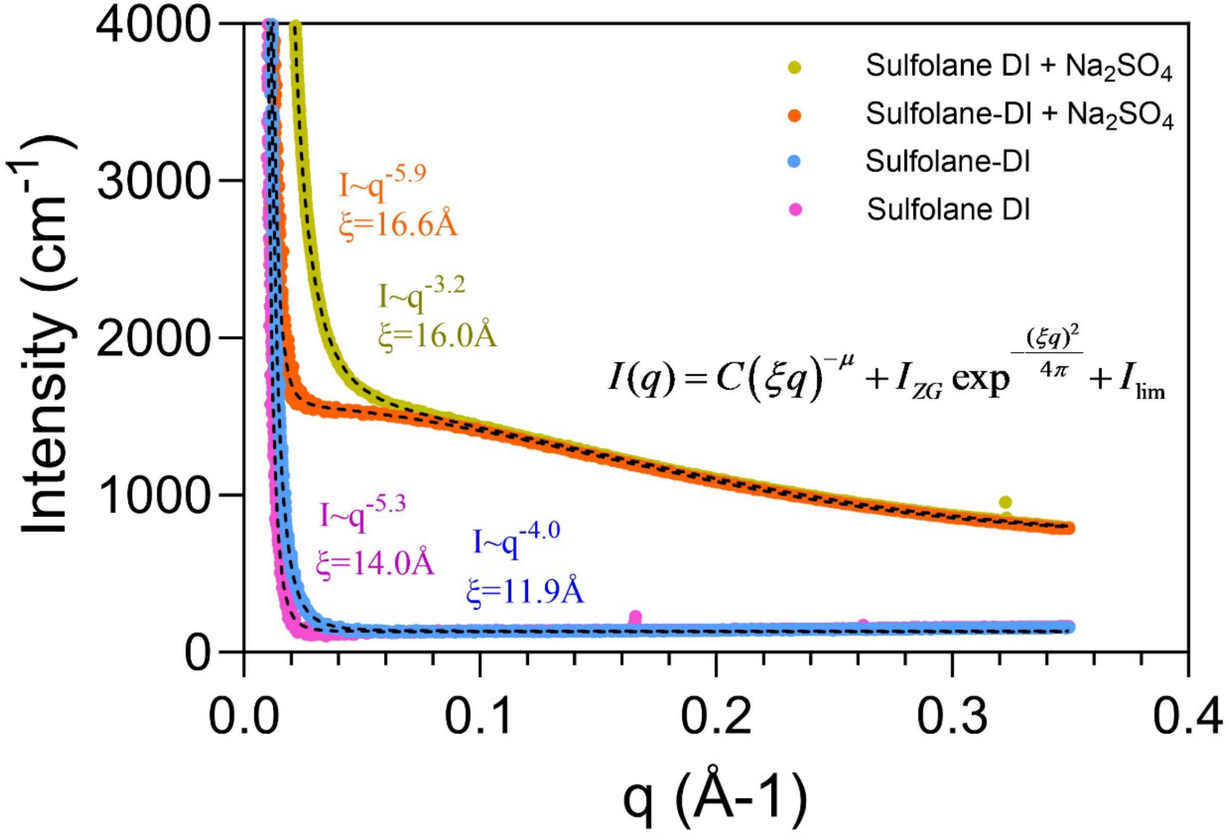
★ **SULFOLANE FLOATS ON THE WATER RICH PHASE, ALTHOUGH IT IS HEAVIER THAN PURE WATER**

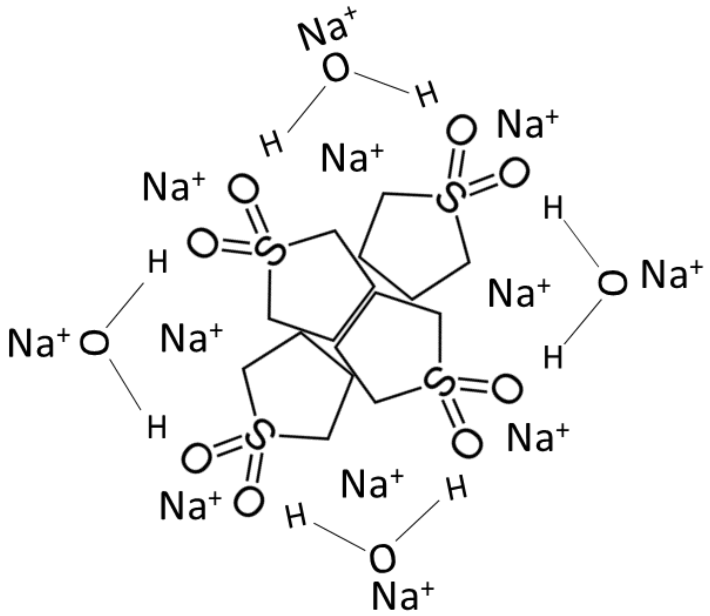
The Water Rich Phase is Viscous and Dense





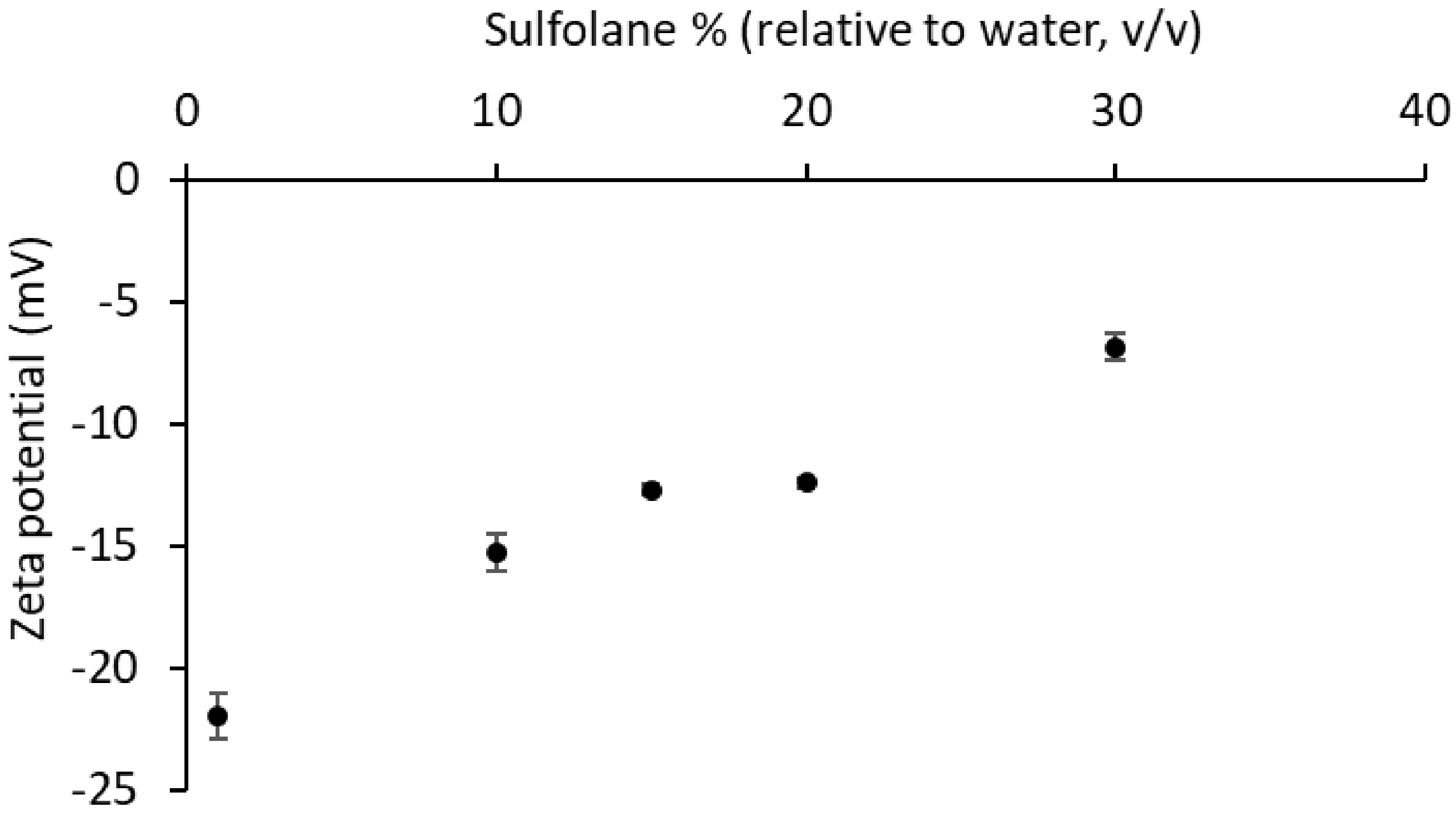
Sulfolane Miscibility in Water





Pensini, E., Marangoni, A.G., Bartokova, B., Fameau, A.L., Corradini, M.G., Stobbs, J.A., Arthur, Z. and Prévost, S., 2024. Sulfolane clustering in aqueous saline solutions. *Physics of Fluids*, *36*(3).

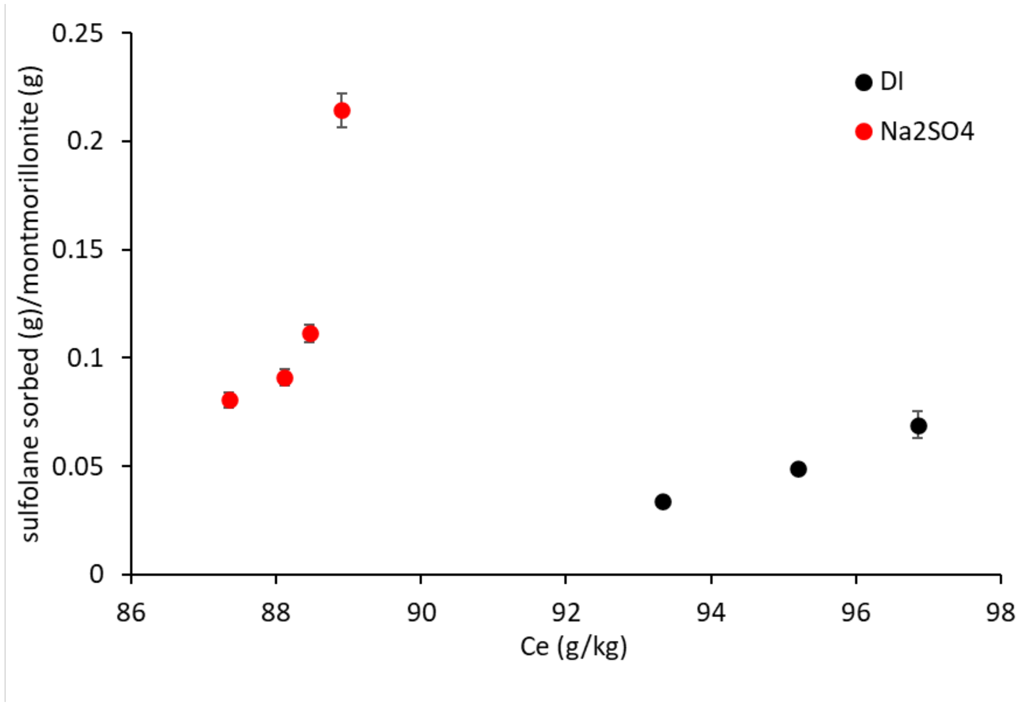
Separated Sulfolane Droplets are Negatively Charged

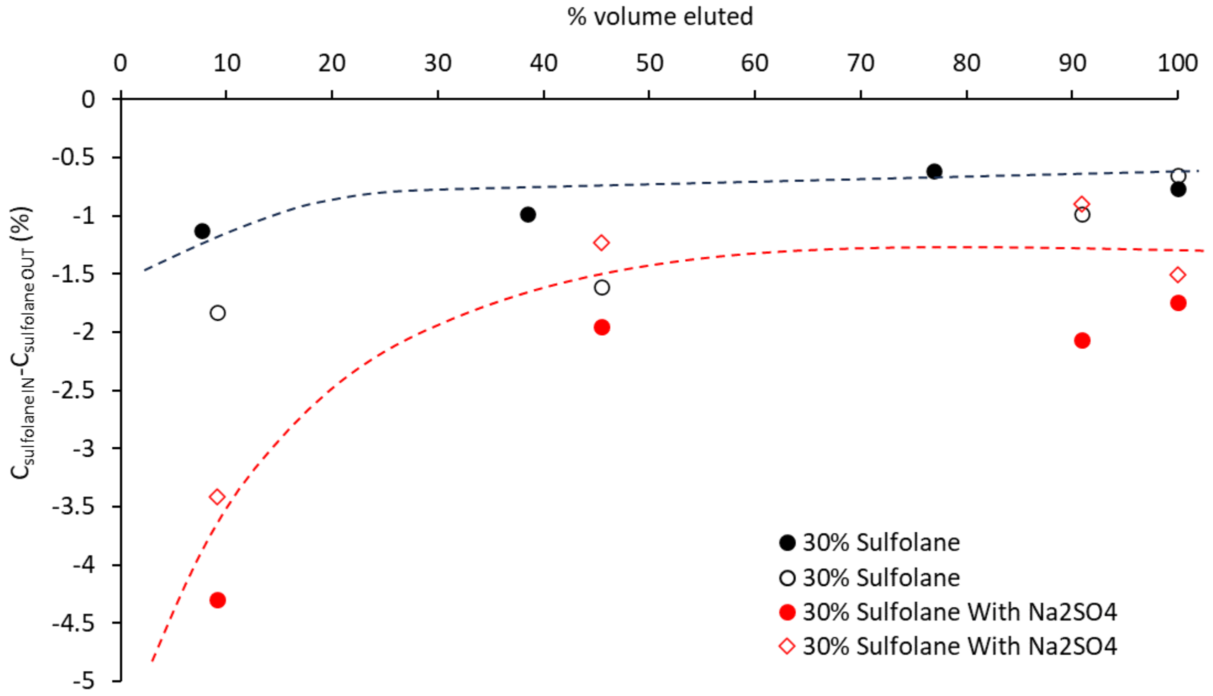


Zeta potential (ζ) of sulfolane droplets in water, emulsified with 0.06 M Na_2SO_4

Effect of Miscibility on Sulfolane Sorption and Migration

- Sulfate salts delay sulfolane migration in model clay fractures and decrease overall mass recovery at the outlet by promoting sorption

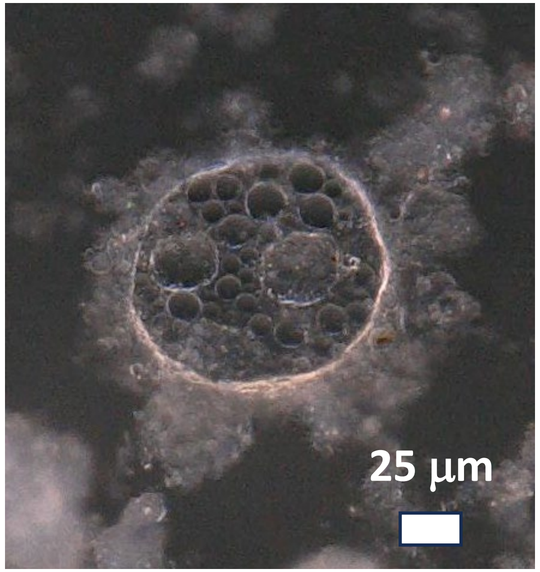




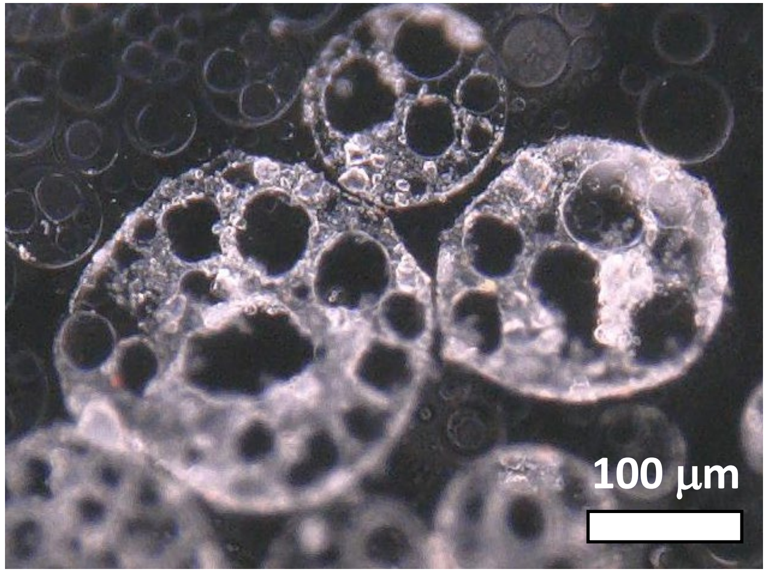
Bartokova, B., Marangoni, A.G. and Pensini, E., 2024. Effect of sulfolane demixing and sorption on its migration through model fractured and porous media. *Water, Air, & Soil Pollution*, *235*(2), p.97.

Effect of Miscibility on Sulfolane Sorption and Migration

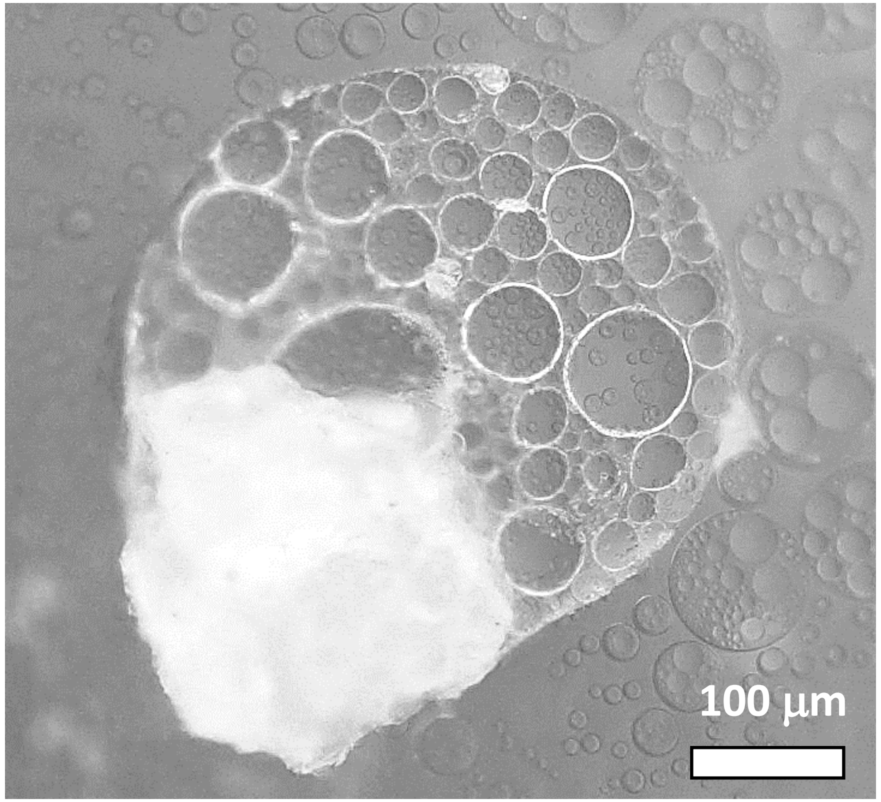
- Sulfates (e.g., Na_2SO_4) also promote sulfolane sorption onto limestone
- Sulfolane sorption onto minerals is limited in pure water



Clay sorbed onto sulfolane emulsified by Na_2O_4

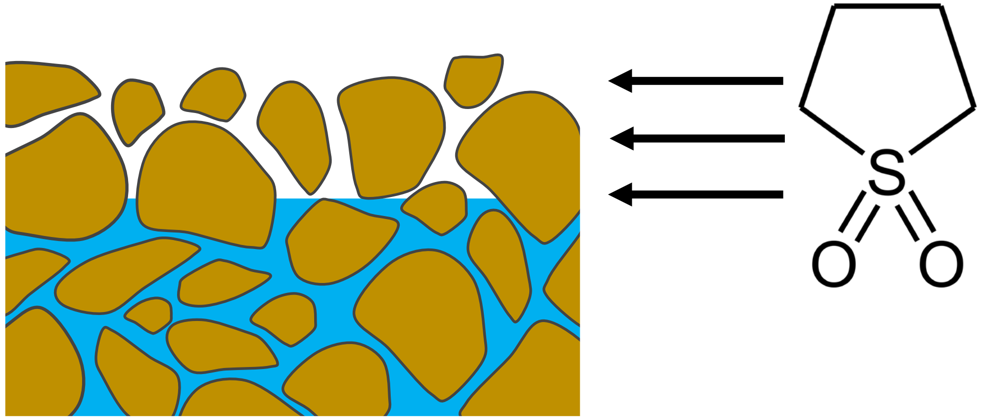


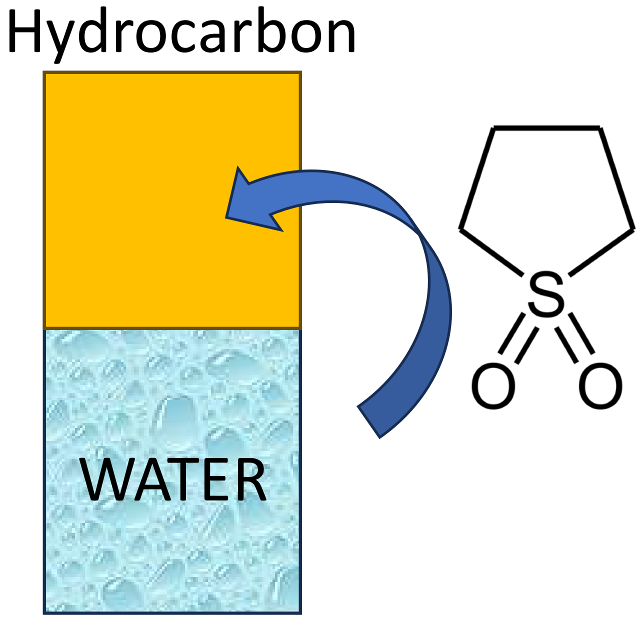
Limestone sorbed onto sulfolane emulsified by Na_2O_4



Effect of Ions on Sulfolane Partitioning between Oil and Water – Implications on Migration

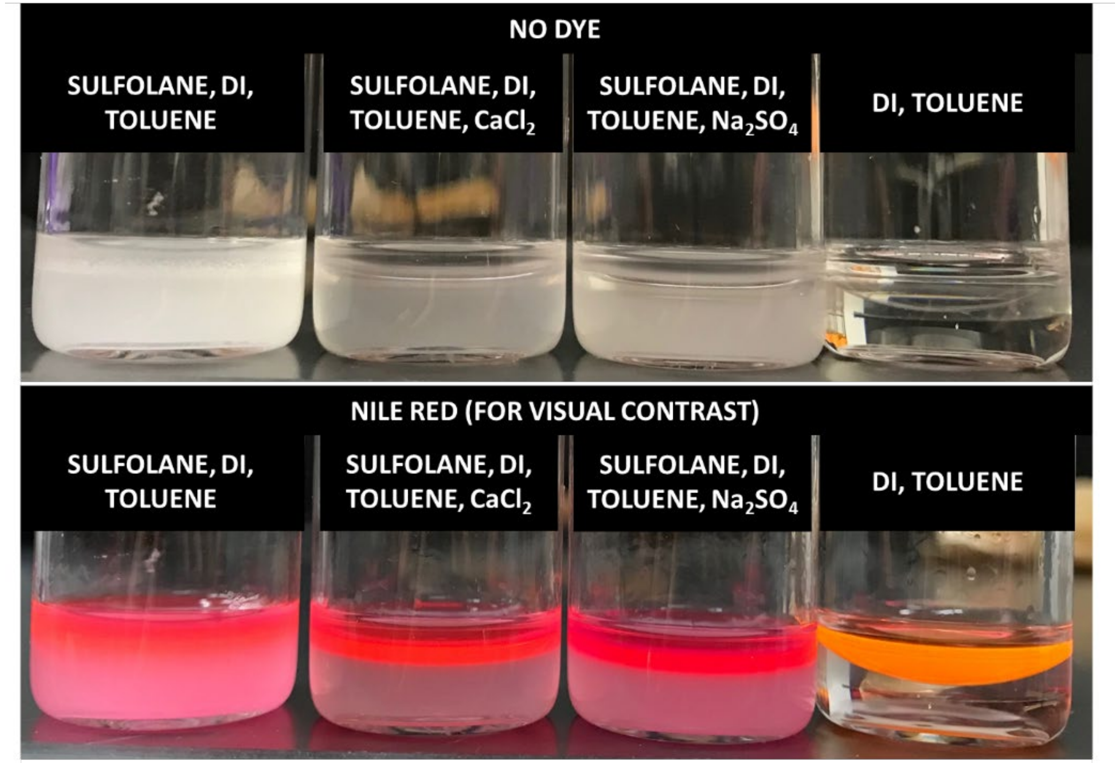
- Sulfate and chloride salts promote sulfolane partitioning into immiscible co-contaminants (e.g. hydrocarbons)
  - Sulfolane can be found above the water table
  - Sulfolane vertical migration in sandy aquifers is delayed





Bartokova, B., Marangoni, A.G., Laredo, T. and Pensini, E., 2023. Phase behavior of sulfolane: Potential implications for transport in groundwater. *Colloids and Surfaces A*, *677*, p.132451.

Without Salts Sulfolane Emulsifies Toluene in Water, Likely Promoting Migration

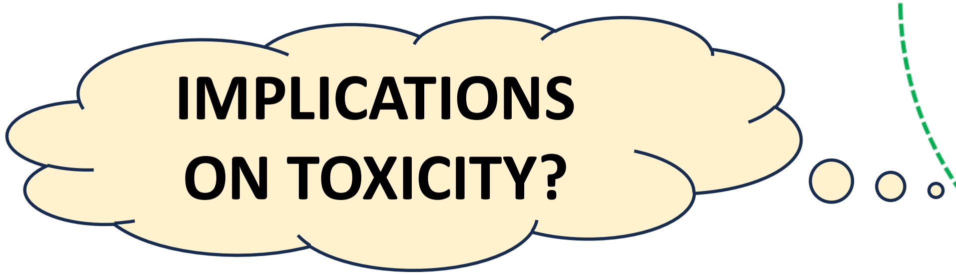


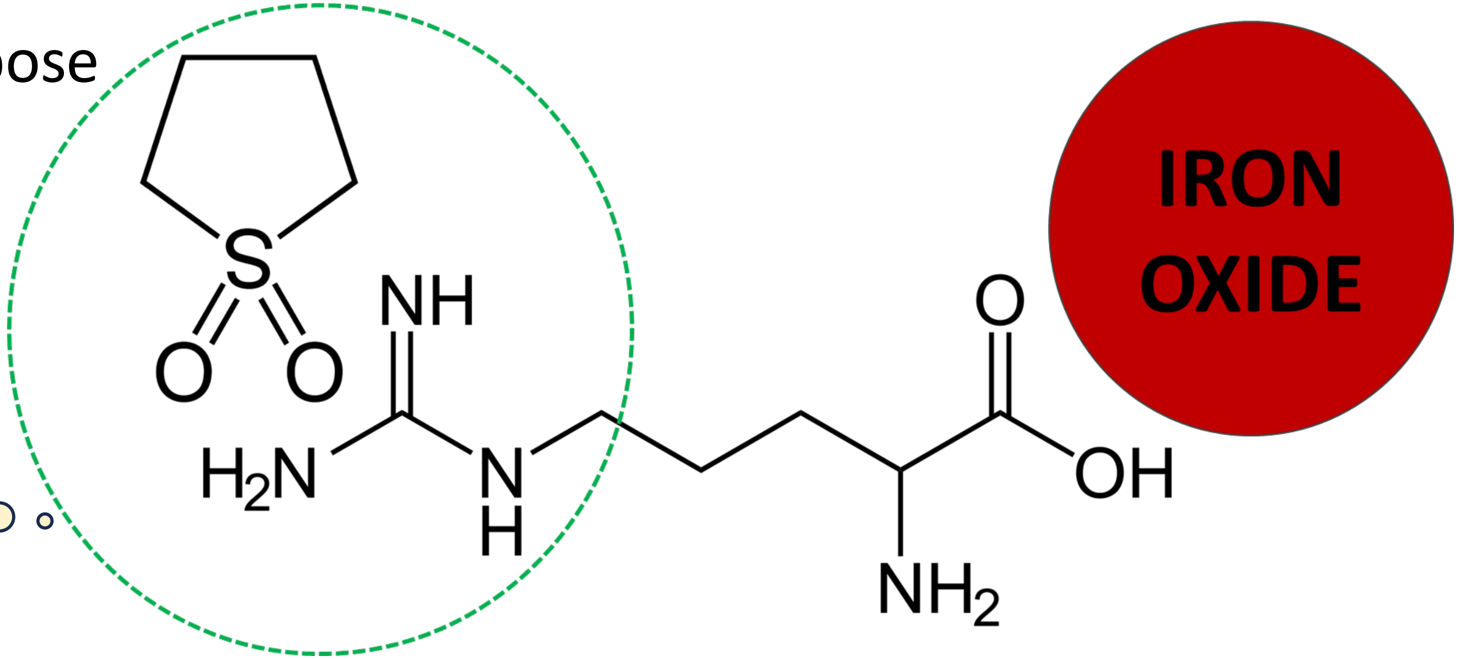
Bartokova, B., Marangoni, A.G. and Pensini, E., 2024. Effect of sulfolane demixing and sorption on its migration through model fractured and porous media. *Water, Air, & Soil Pollution*, *235*(2), p.97.

Sulfolane Sorption onto Minerals – Effect of Amino Acids (Due to Hydrocarbon-Degrading Bacteria)

- Amino acids (present due to bacterial activity) foster sulfolane sorption onto iron oxides

Based on IR data, we propose HN…SO interactions





*Erica Pensini, Caitlyn Hsiung, and Nour Kashlan. Arginine 'Linker' Enhances Sulfolane Sorption onto Iron Oxide. Colloids Surfaces C (2024), submitted.

Sulfolane Partitioning– Effect of Bacterial Activity

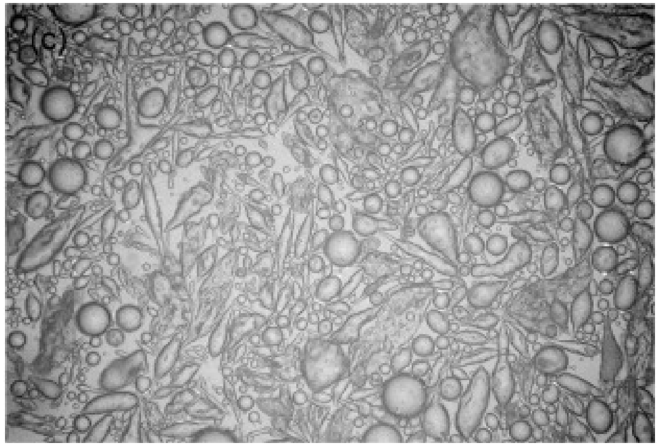
Do amino acids, proteins and bacterial biosurfactants generated during bacterial activity affect sulfolane miscibility in water?

- Rhamnolipids (bacterial biosurfactants) demix tetrahydrofuran from water

  Source: Patel, V., Marangoni, A.G., Ghazani, S.M., Laredo, T., Stobbs, J. and Pensini, E., 2023. Effect of bacterial surfactants on the phase behavior of miscible pollutants in water. Colloids and Surfaces C, 1, p.100013.

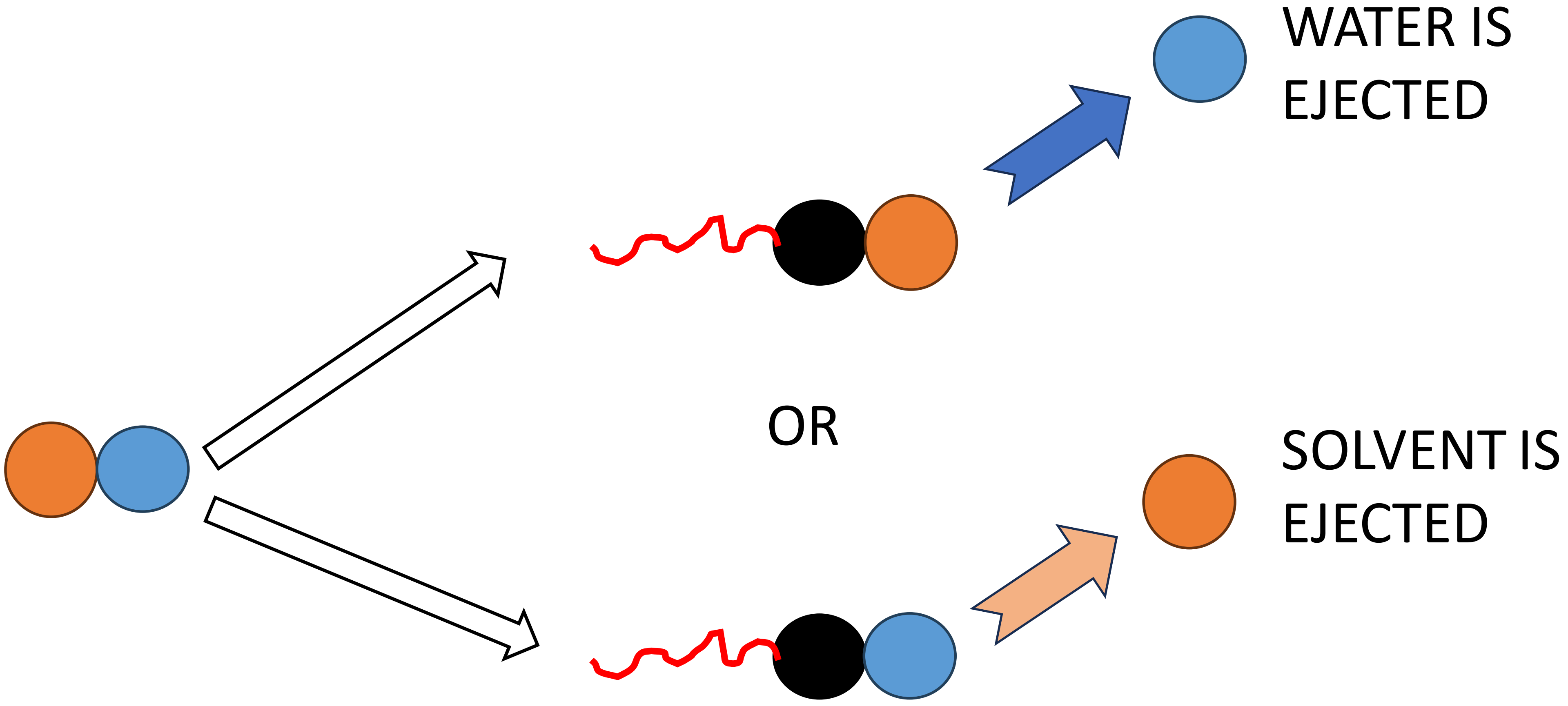
- We are testing sulfolane solubility in water in the presence of active diesel-degrading cultures, which produce biosurfactants, amino acids etc.

Diesel emulsified by bacterial biosurfactants



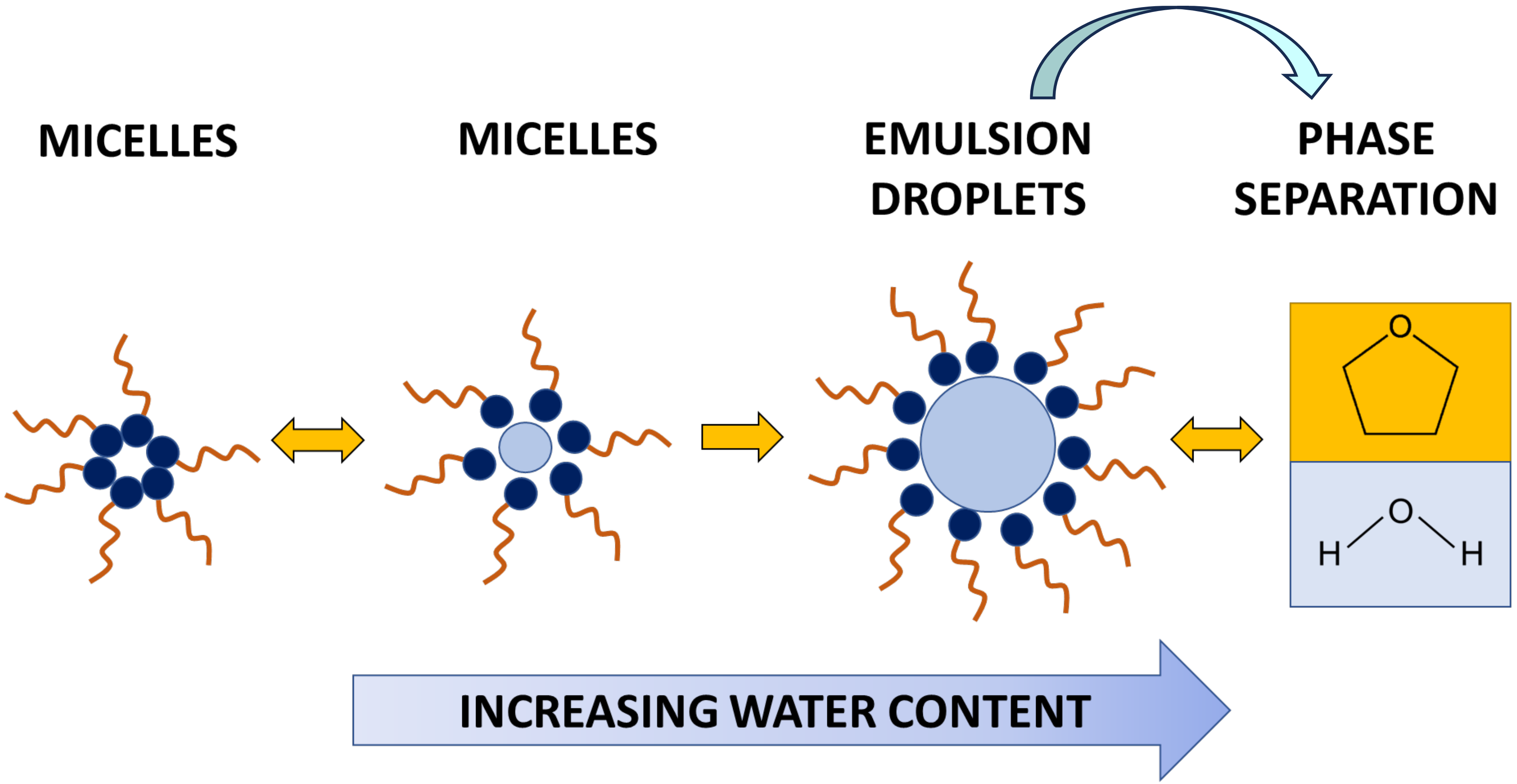
Source: Marshall, T., Paschos, A., Marangoni, A.G., Yang, F. and Pensini, E., 2021. Injectable cationic traps and sticky bacterial emulsifiers: A safe alliance during diesel bioremediation. Colloids and Surfaces A, 613, p.126051.

How do Surfactants Induce Separation?



How do Surfactants Induce Separation?

DROPLET COALESCENCE IS RELATED TO SURFACTANT SELF ASSEMBLY

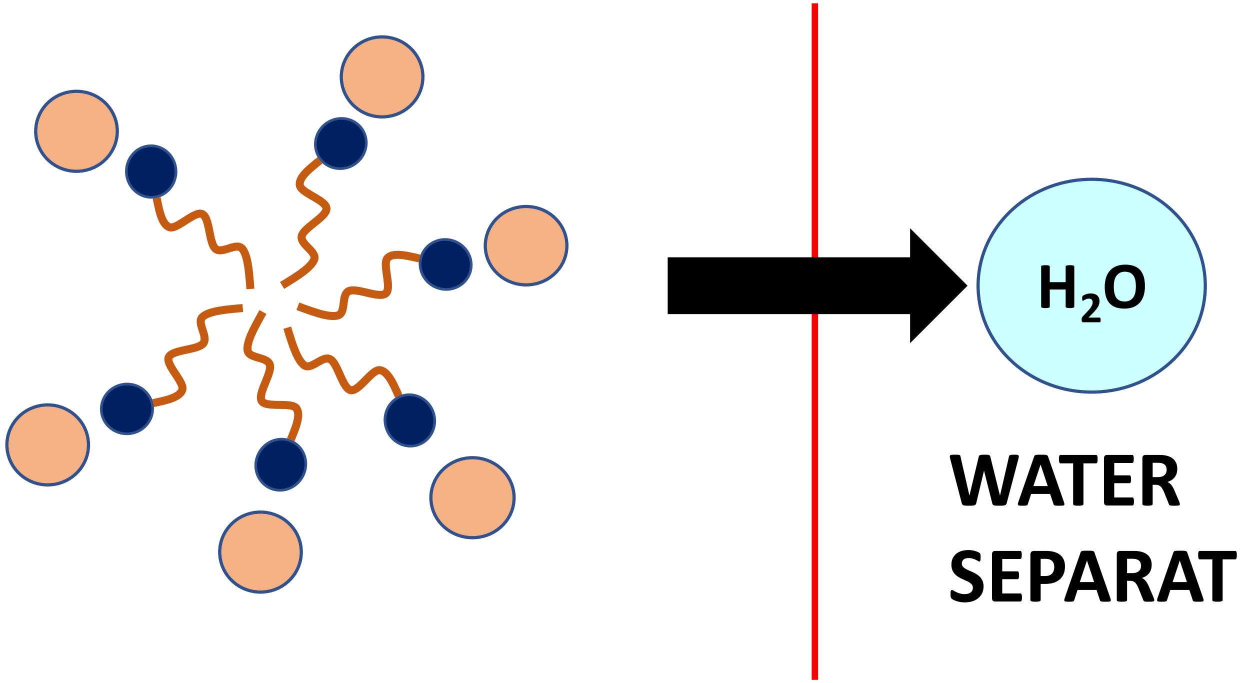


Dynamic process: when one solvent goes in the other, the process resumes

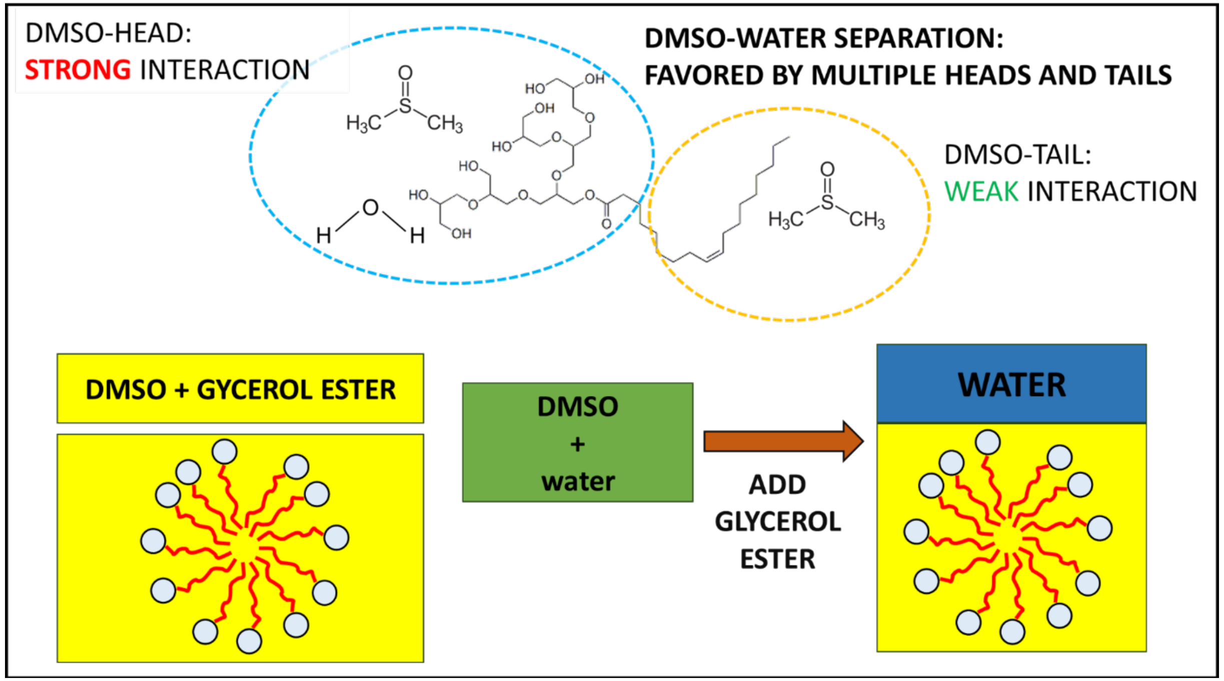
SURFACTANT HEAD PRIMARILY INTERACTS WITH WATER

How do Surfactants Induce Separation?

HEADS INTERACT STRONGLY WITH SOLVENT

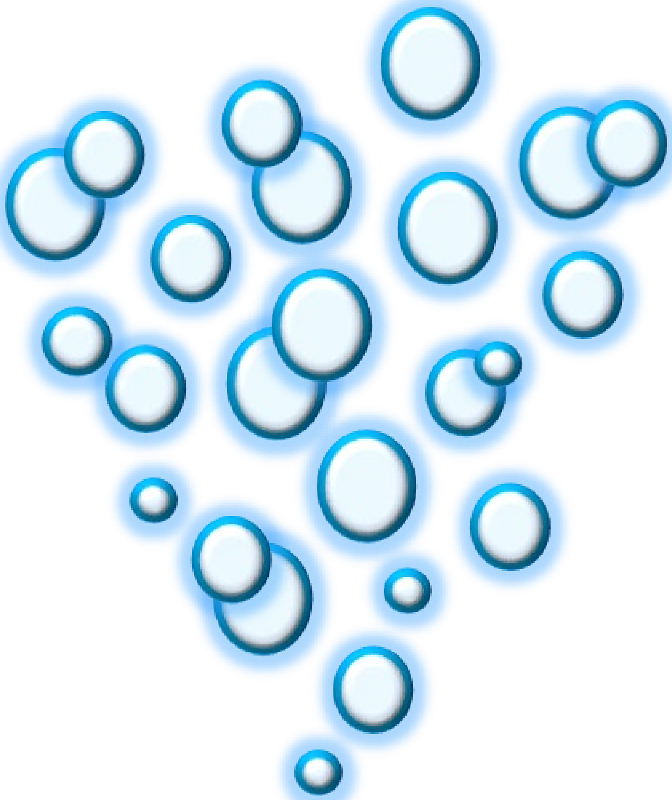


WATER SEPARATION

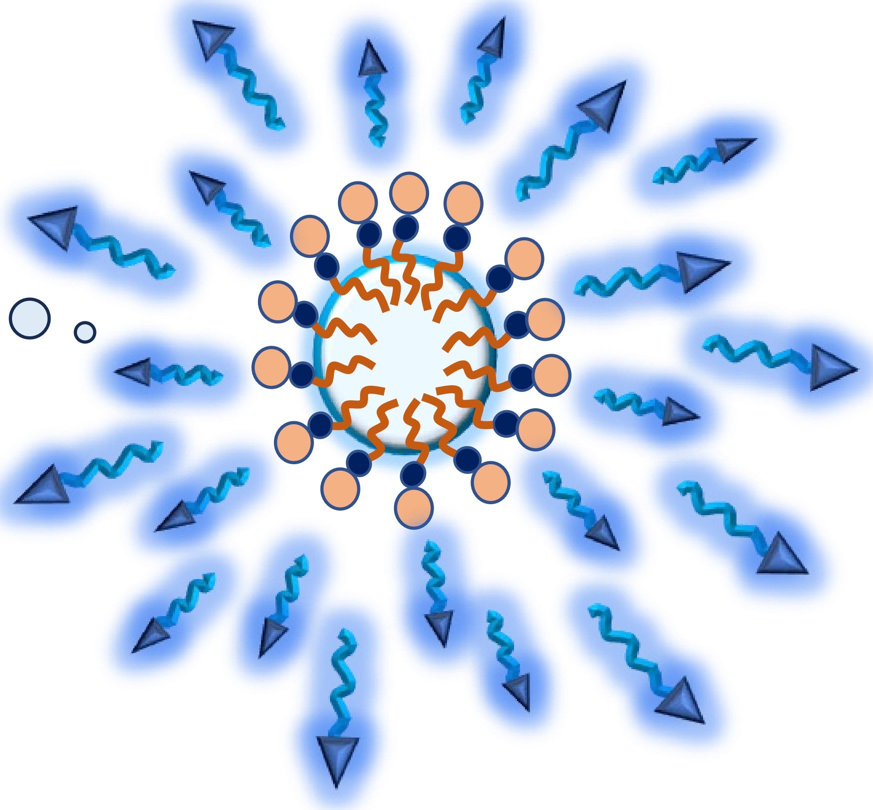


Bartokova, B., Marangoni, A.G. and Pensini, E., 2024. Role of heads and tails on tetrahydrofuran-and dimethyl sulfoxide-water separation by glycerol and sucrose esters. *Physics of Fluids*, *36*(7).

Can We Harness Surfactants for Sulfolane Remediation?



SURFACTANT-SULFOLANE COMPLEX



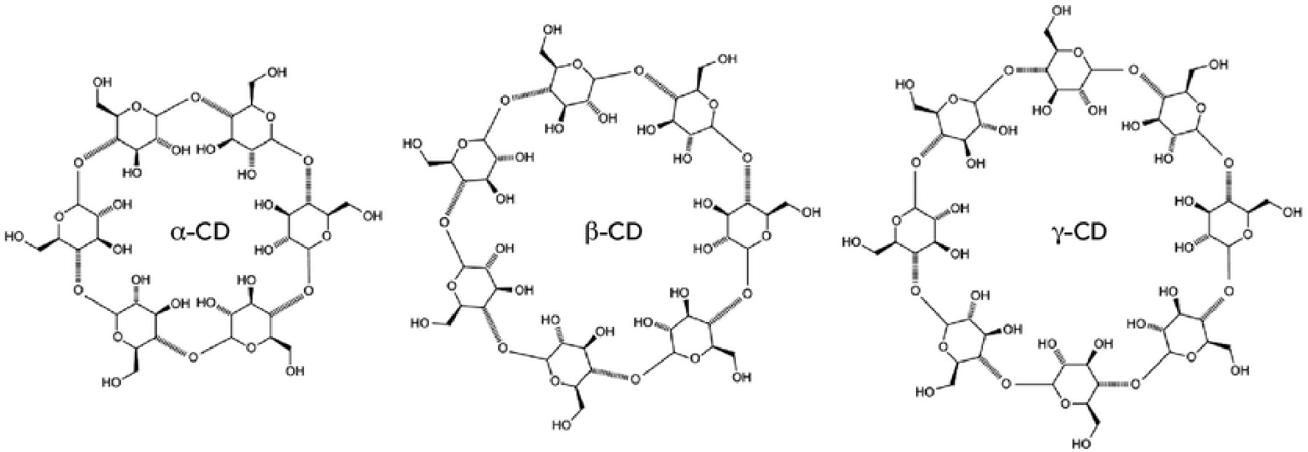
AIR SPARGING+
SURFACTANT

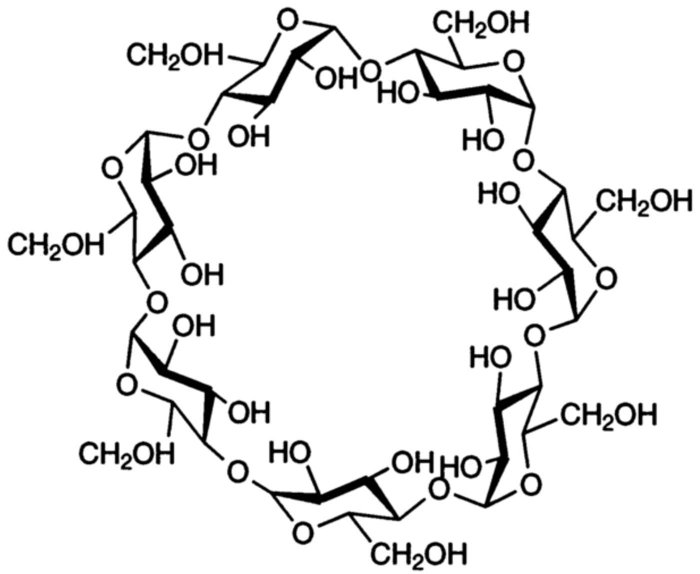
ENHANCED WATER EVAPORATION FROM AIR-LIQUID INTERFACE

SULFOLANE ACCUMULATION ON AIR BUBBLES

*Ongoing research – Caitlyn Hsiung

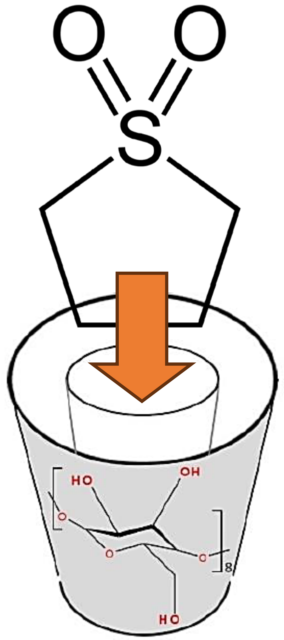
Removal of Sulfolane by Cyclodextrin

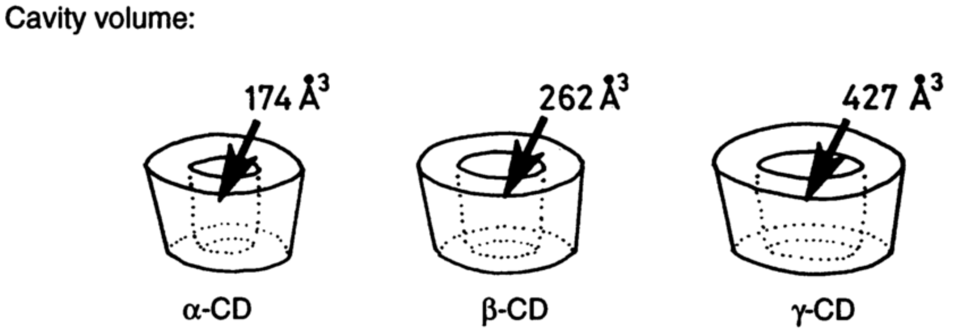




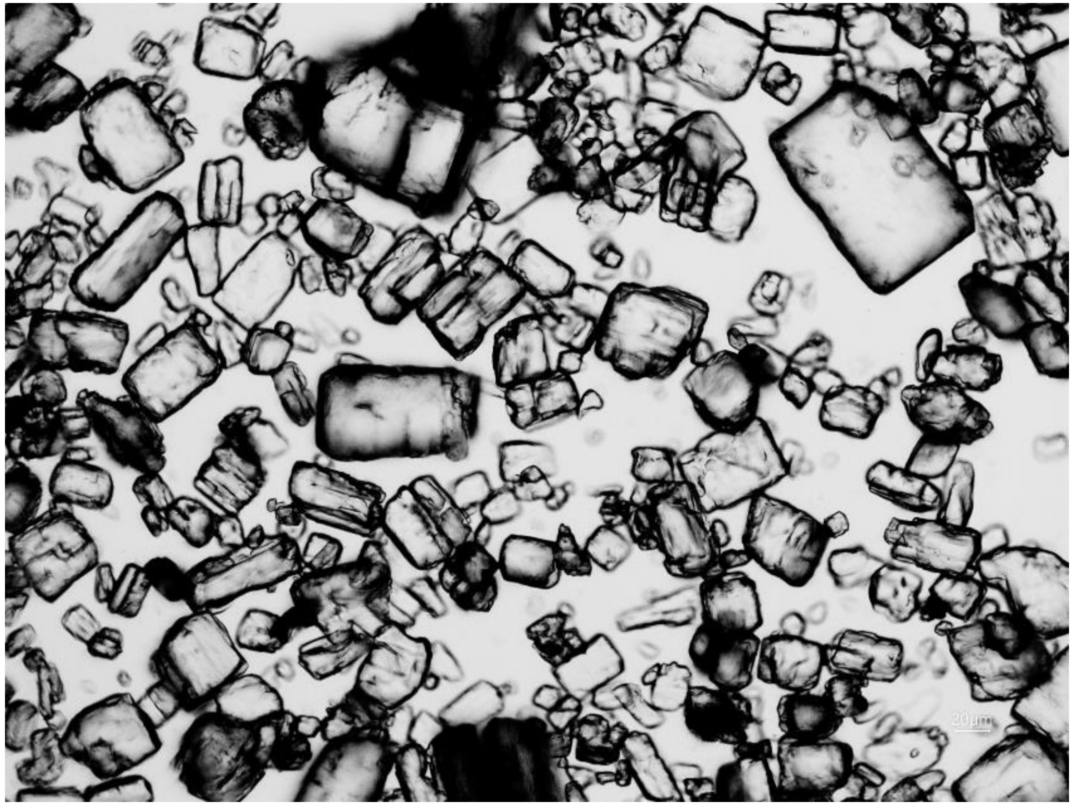
- Inside of the ‘basket’ is hydrophobic, outside is hydrophilic

- We can pick the right basket ‘size’ to fit in sulfolane

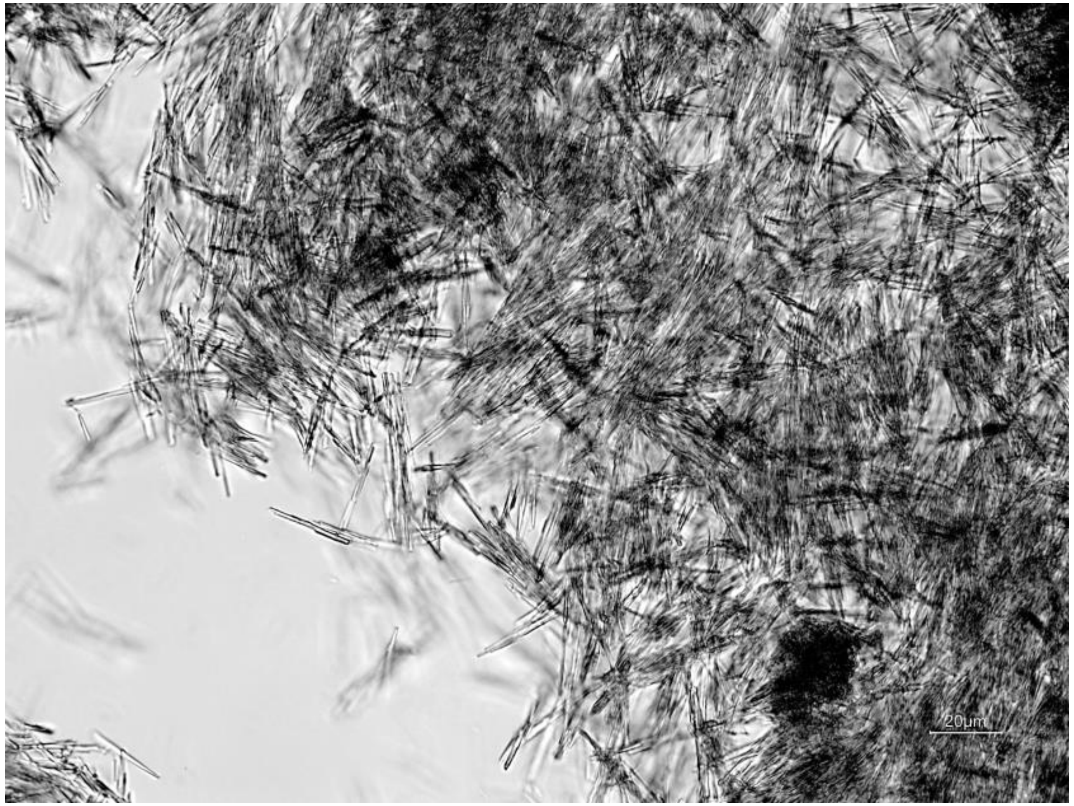




Removal of Sulfolane by Cyclodextrin



alfa cyclodextrin in water



alfa cyclodextrin in sulfolane-water

≈80 mg sulfolane removed/g cyclodextrin

Can We Harness Surfactants for Sulfolane Remediation?

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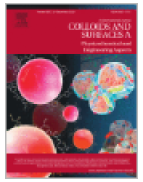
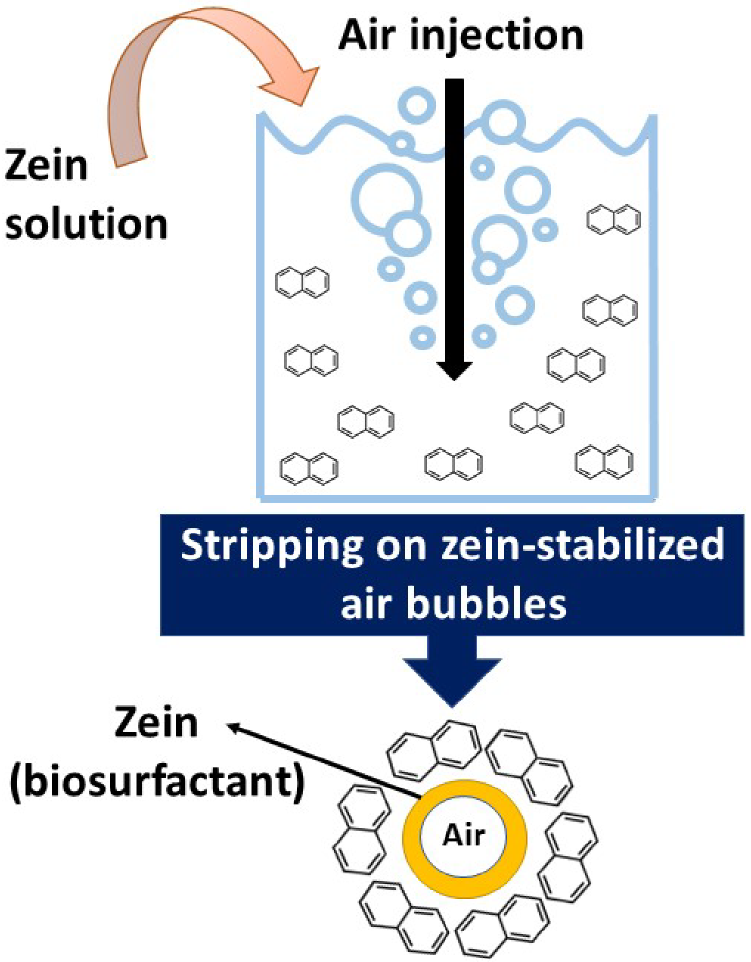
Colloids and Surfaces A: Physicochemical and Engineering Aspects

Volume 607, 20 December 2020, 125518



Laccase-zein interactions at the air-water interface: Reactors on an air bubble and naphthalene removal from water

Tatianna Marshall [a], Alejandro G. Marangoni [b], Thamara Laredo [c], Klaudine M. Estepa [a], Maria G. Corradini [b d], Loong-Tak Lim [b], Erica Pensini [a]



Amines are Found Alongside Sulfolane

- Alkanolamines and diisopropylamine (DIPA) are used alongside sulfolane for carbon capture and storage, and to sweeten sour gas
- They are also found in cosmetic formulations and household products (without sulfolane)
- In the absence of adequate wastewater treatment, we can expect them to migrate in groundwater

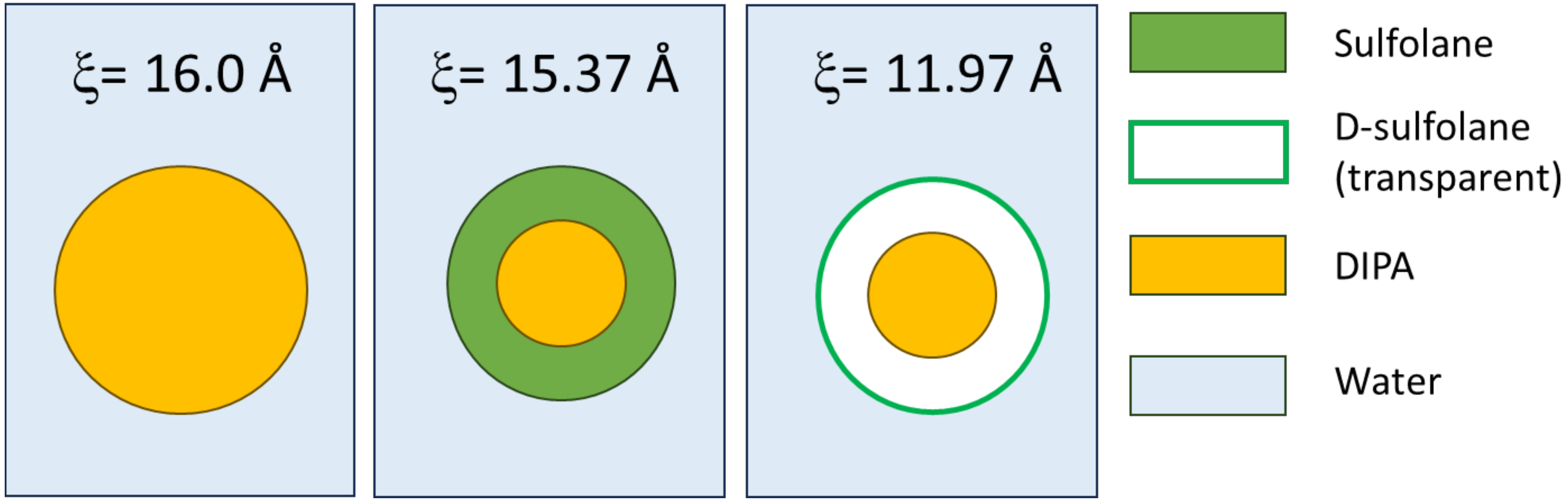
DIPA Sorbs onto Minerals Even Without Salts, but Only Without Sulfolane

	DIPA **(g DIPA/g sorbent)**	**Sulfolane** **(g sulfolane/g sorbent)**
Clay	0.23±0.04	0.05±0.01
Limestone	0.22±0.03	Negligible
Iron oxide	0.18±0.02	Negligible
Gypsum	0.21±0.02	Negligible

SALTS LIKELY CHANGE THIS SCENARIO

(Study with other amines will follow)

Sulfolane Solubilizes DIPA in Water, Without Salts



SALTS LIKELY CHANGE THIS SCENARIO

Study with sulfolane and other amines is ongoing

* Erica Pensini, Alejandro G. Marangoni, Sylvain Prevost. Sulfolane facilitates diisopropylamine dissolution in water, potentially enhancing pollutant transport. Journal of Molecular Liquids (2024), under review.

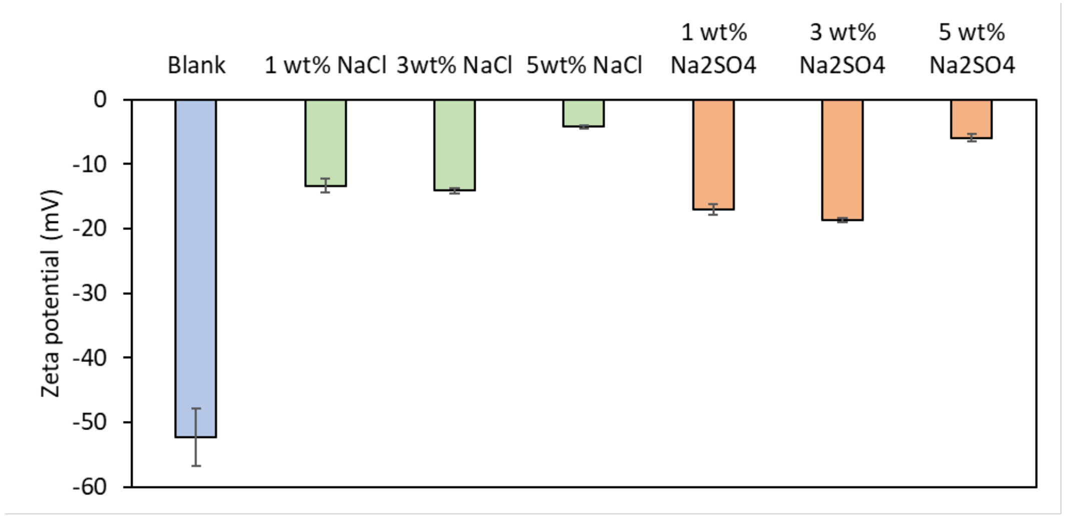
Properties of Amine Mixtures with Water

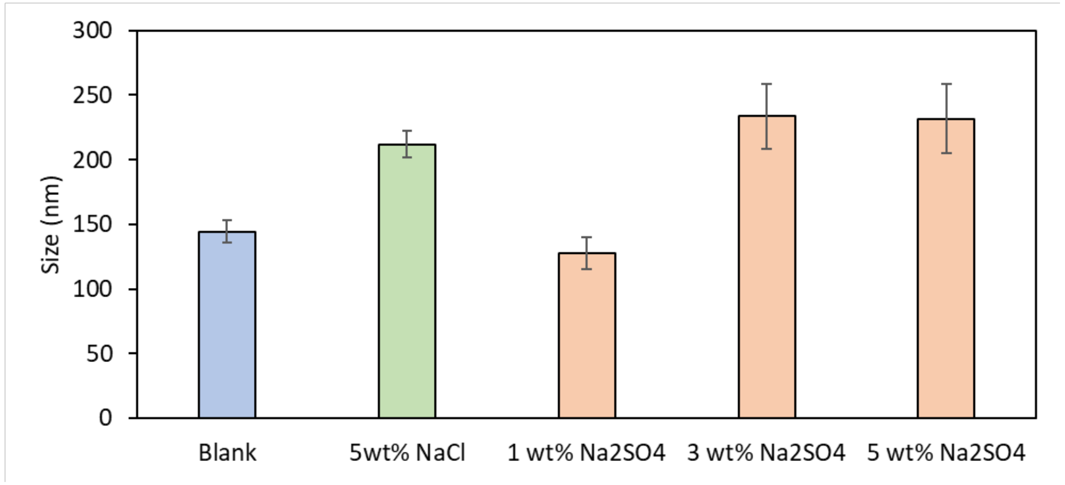
- Alkanolamines are soluble in pure water, DIPA yields dispersions (nano-sized droplets)
- Salts further decreases DIPA miscibility in water

		DIPA wt%								
Salt	**wt% salt**	**10**	**20**	**30**	**40**	**50**	**60**	**70**	**80**	**90**
NaCl	1	1L	1L	1L	1L	2L	2L	2L	2L	2L+S
NaCl	2	1L	1L	2L	2L	2L	2L	2L	2L	2L+S
Na_2SO_4	1	1L	1L	2L	2L	2L	2L	1L+S	1L+S	1L+S
Na_2SO_4	2	1L	2L	2L	2L	2L	2L+S	1L+S	1L+S	1L+S

Salts Decrease the Solubility of DIPA in Water

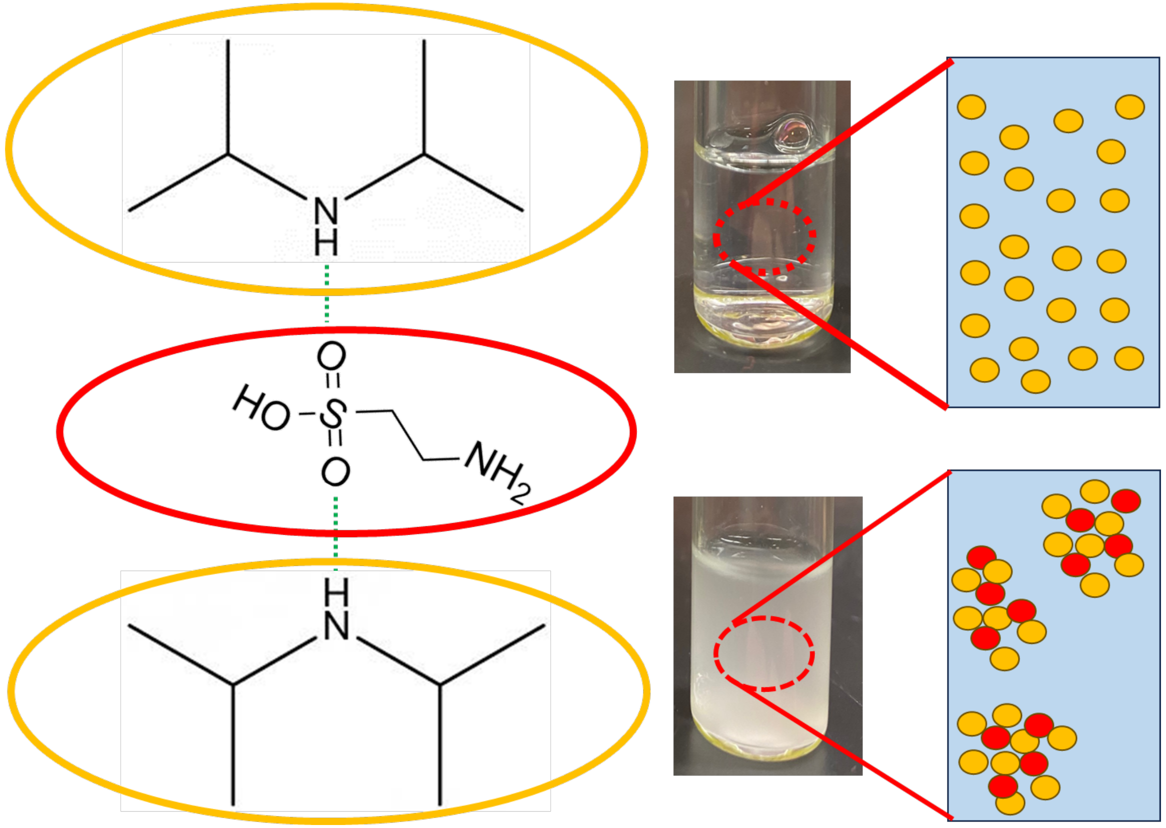
- Sulfate and chloride salts decrease the miscibility of DIPA in water





- 1wt% DIPA in water

Taurine Decreases the Solubility of Amines in Water

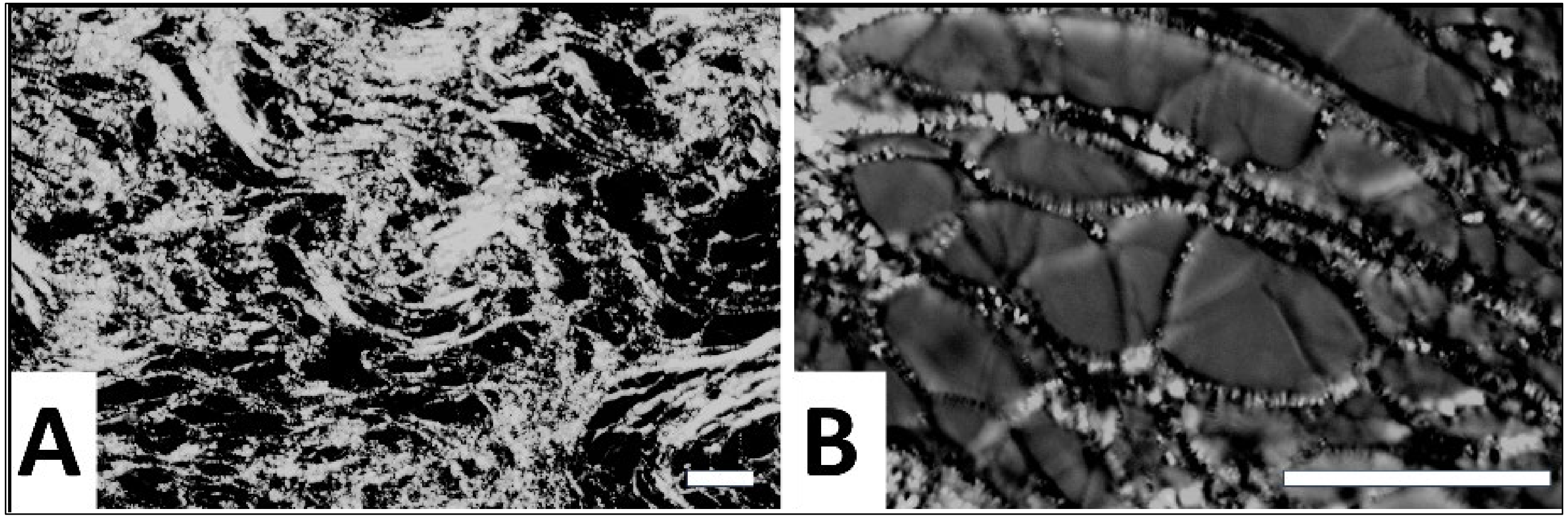


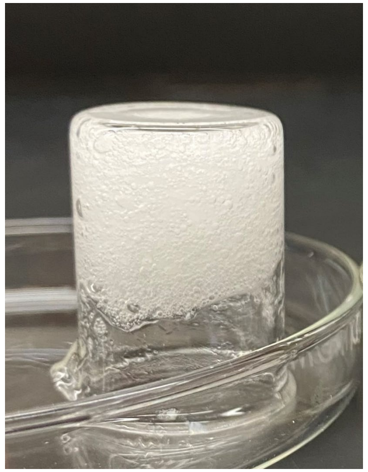
- The effect is most marked with DIPA, but it is also seen with alkanolamines

IMPLICATIONS ON TOXICITY?

Erica Pensini, Caitlyn Hsiung, and Nour Kashlan. Potential Toxic Effects Linked to Taurine Interactions with Alkanolamines and Diisopropylamine. Discover Water (2024), accepted.

Interactions between Carboxylic Acids and Amines: Gelation by Fatty Acids



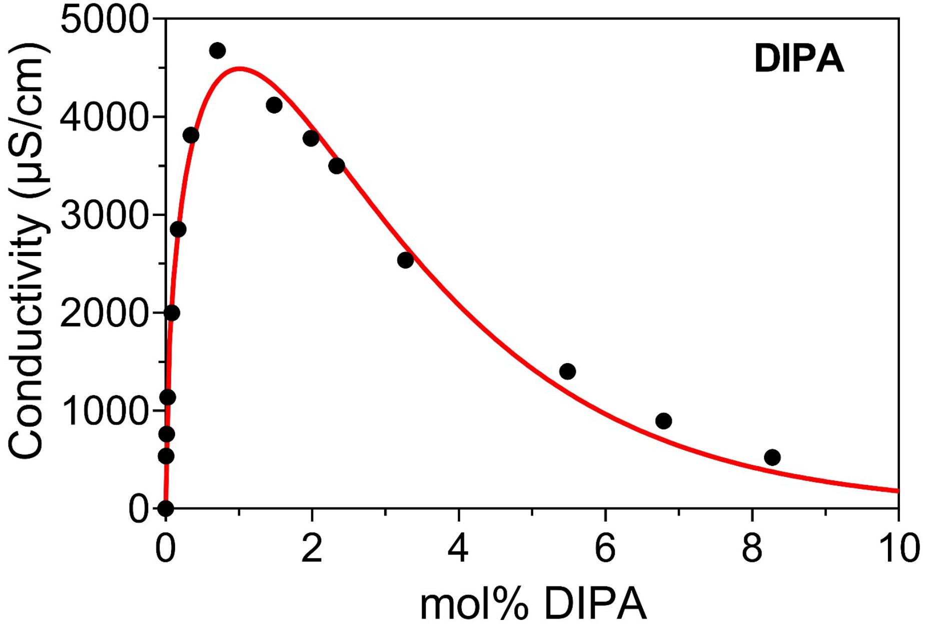


Pensini, E., Gregori, S., Marangoni, A. G., Ghazani, S. M., Su, Z., Chen, A., & Kashlan, N. (2024). Ethanolamine piezoelectric hydrogels structured by oleic acid lamellae. Journal of Molecular Liquids, 397, 124185.

Erica Pensini, Peter Meszaros, Nour Kashlan, Alejandro G. Marangoni, Stefano Gregori, Saeed Mirzaee Ghazani, Joshua van der Zalm, Aicheng Chen. Ferroelectric soft materials formed with alkanolamines and unsaturated fatty acids. Journal of Molecular Liquids (2024), revision requested.

Properties of Amine Mixtures with Water- Potential for Electrokinetic Treatment

- Solutions and mixtures of DIPA and alkanolamines are electrically conductive, rendering electrokinetic separation a viable approach



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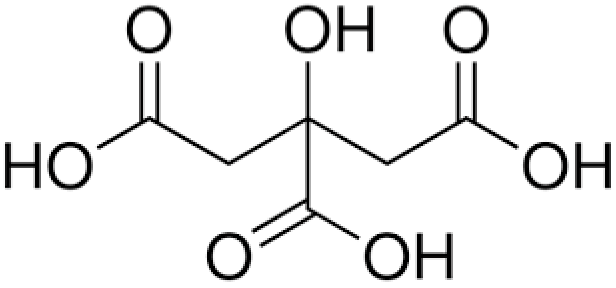
Colloids and Surfaces C: Environmental Aspects
Volume 2, 1 November 2024, 100026

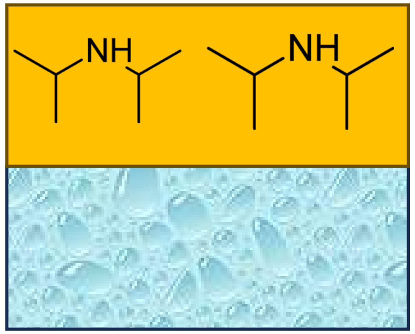
Mixing behavior and electrical conductivity of diisopropyl amine-water surfactantless emulsions: Implications for the electrokinetic purification of water

Matthew Sing [a], Alejandro G. Marangoni [b], Erica Pensini [a c]

Interactions between Carboxylic Acids and Amines



Citric acid ejects DIPA from water



*Ongoing research – Nour Kashlan

In a Nutshell: Water Chemistry and Co-Contaminants are Key to Miscibility, Sorption and Migration!

- Salts demix sulfolane from water, promote its sorption onto minerals and hamper its migration
- Amino acids promote sulfolane sorption onto iron oxides
- Salts oppose hydrocarbon solubilization by sulfolane
- Salts demix DIPA from water, while sulfolane enhances its solubility in pure water
  - Solubility with salts and alkanolamines has yet to be studied
- The amino acid taurine decreases DIPA miscibility
- Carboxylic acids affect the miscibility of DIPA in water and fatty acids gel alkanolamines in water

THANK YOU!

Grad Students wanted!

PENSINI LAB
University of Guelph

Bibiana Bartokova

Nour Kashlan and Caitlyn Hsiung

Peter Meszaros

Saeed Ghazani

NSERC
CRSNG

Shell

Matrix Solutions Inc.
A Montrose Environmental Company

Key Collaborator: Alejandro Marangoni

Canadian Light Source
Centre canadien de rayonnement synchrotron

Adam Leontowich, Jarvis Stobbs, Amanda Quirk, Scott Rosenthal, Zach Arthur

NEUTRONS FOR SOCIETY

Sylvain Prevost

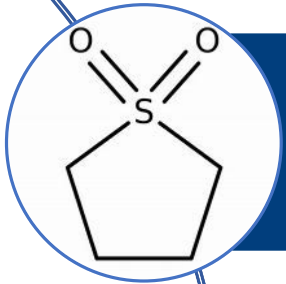
AZIMUTH

Geosyntec consultants

Development and Demonstration of Site-Specific Sulfolane Management and Remediation Strategies

Sarah Walker, PhD. PG.
Srinivasa Varadhan, PhD. PE. PEng

Agenda



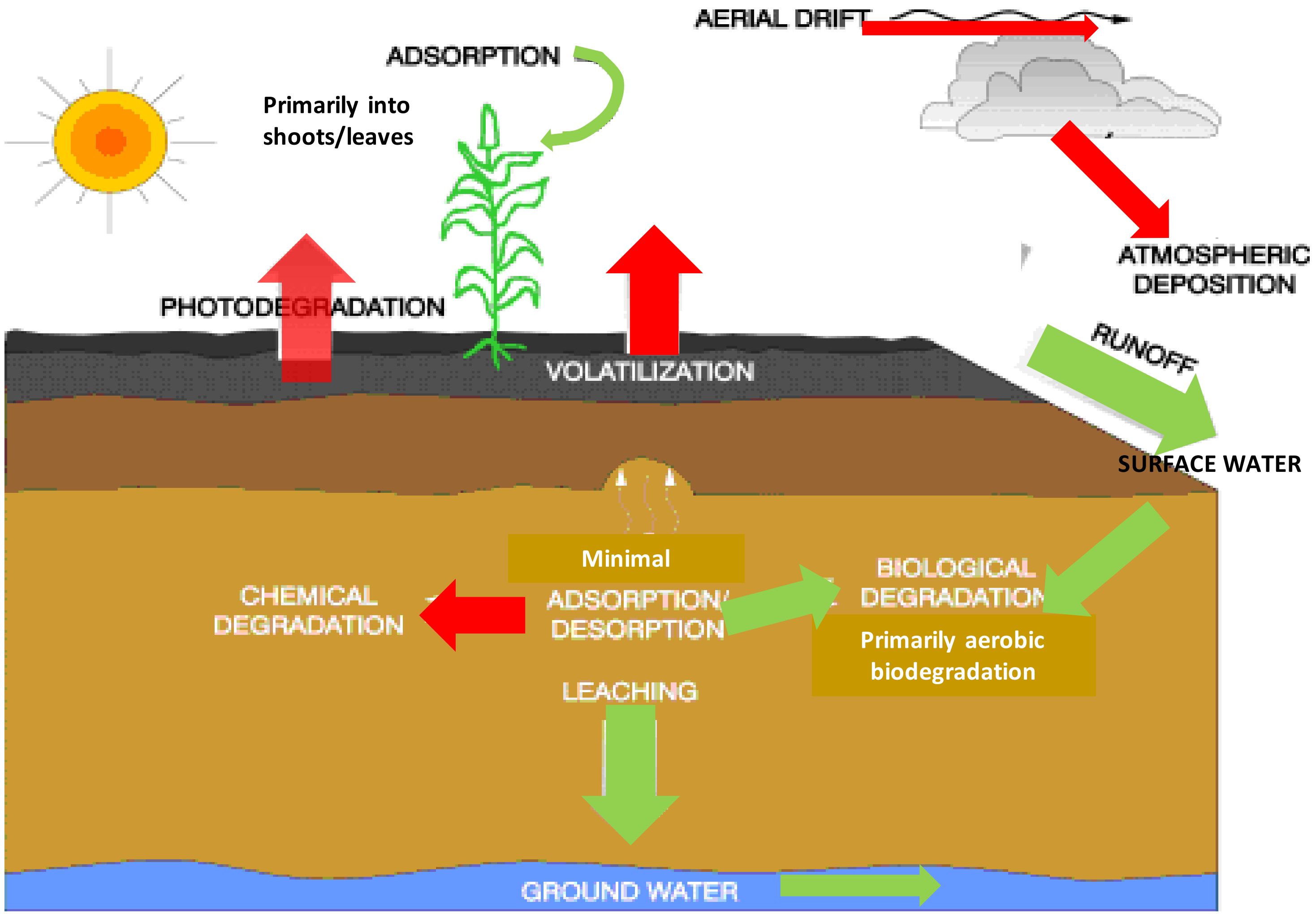
Sulfolane Overview

Demonstrated Case Studies

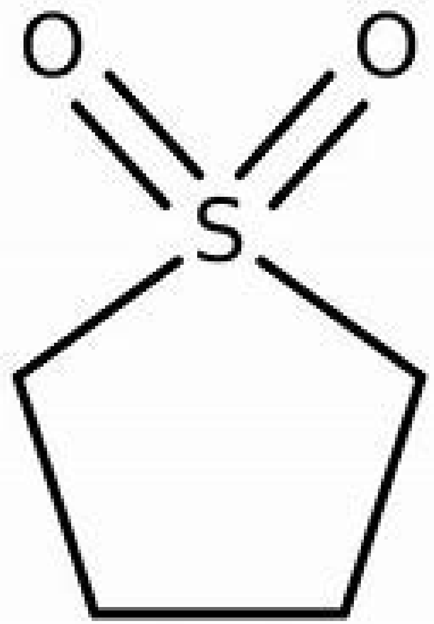
Key Takeaways

Geosyntec consultants

SULFOLANE OVERVIEW



AERIAL DRIFT
ADSORPTION
Primarily into shoots/leaves
ATMOSPHERIC DEPOSITION
PHOTODEGRADATION
VOLATILIZATION
RUNOFF
SURFACE WATER
Minimal
ADSORPTION/ DESORPTION
CHEMICAL DEGRADATION
BIOLOGICAL DEGRADATION
Primarily aerobic biodegradation
LEACHING
GROUND WATER



O
O
S

$(CH_2)_4SO_2$

State of Science – Sulfolane Remediation

Technology	Mechanism	Full-scale	Pilot	Laboratory
GAC Sorption (Case Study 1 & 4)	Physical	California (gw)	--	--
Ex-situ Aerobic Bioremediation (Case Study 3)	Biological	California (gw)	Alberta (gw/soil)	Alaska (gw), Taiwan (gw)
In-situ Aerobic Bioremediation (Case Study 4)	Biological	California (gw)	--	--
Anaerobic Bioremediation	Biological	--	--	Australia (gw), Canada (gw)
Soil Washing/Advanced Oxidation Processes (AOP)	Physicochemical	--	--	Canada? (soil/gw)
In-situ Chemical Oxidation	Physicochemical	--	Taiwan (gw)	Alberta (gw), Taiwan (gw)
Phytoremediation	Biological	--	--	Source unknown (gw)

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DEMONSTRATED CASE STUDIES

Fixed Bed Bioreactor

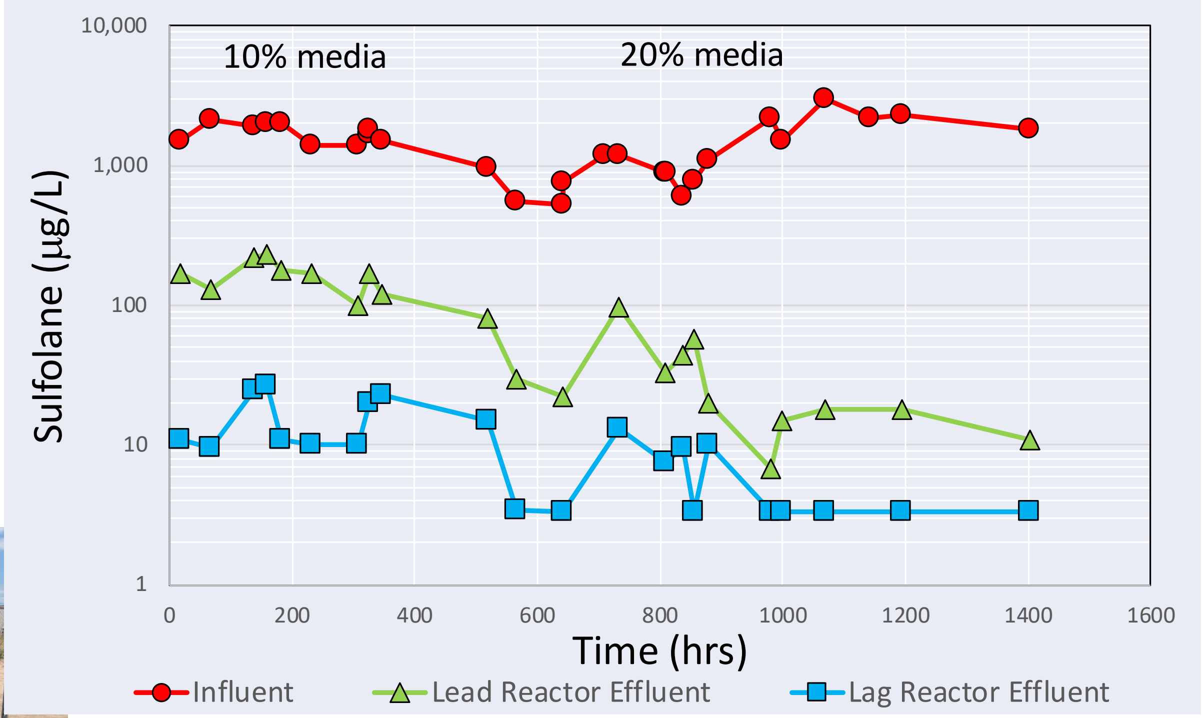
- Uses granular activated carbon (GAC) as a medium for fixed biofilm growth
- Effective for large sulfolane loading
- May require management of biomass through backwashing and for GAC hydraulics
- GAC serves dual purpose by sorbing some sulfolane and potentially increasing treatment capacity

Moving Bed Bioreactor (MBBR)

- Conventional wastewater MBBR technology for groundwater
- Mixed constituent setting: Fumigants, ammonia, high TDS
- Sulfolane removal 1,000 (parts per billion) ppb to less than the detection limit (3.3 ppb)

Moving Bed Bioreactor

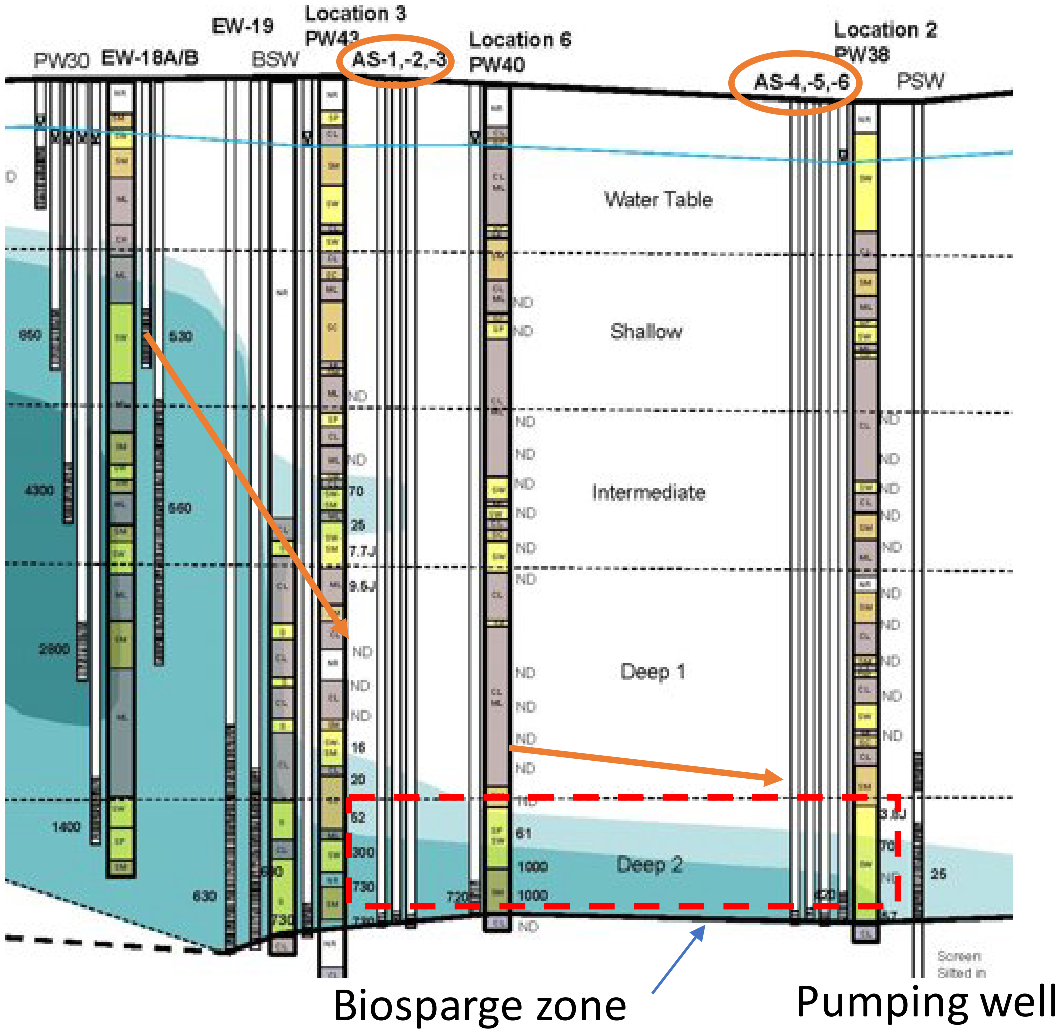
- Laboratory and field piloting
- Parameter optimization
  - Microbial inoculum
  - Nutrient requirements
  - Water quality modification
  - Sensitivity testing
  - Effect of mixed constituent
- Pre/Post-Treatment needs
- O&M optimization



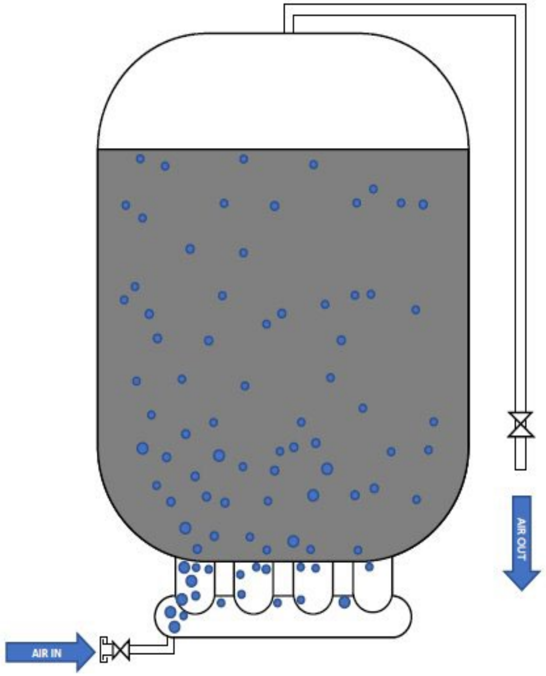
Biosparging

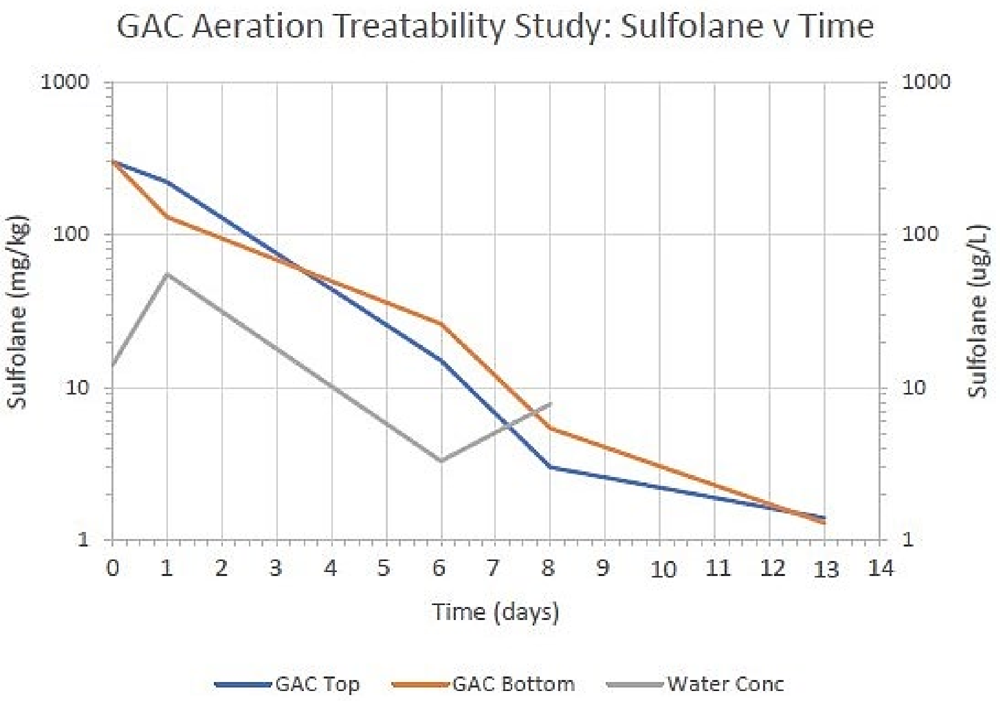
- Pulsed oxygen sparging @ 240' bgs
  - Reduce sulfolane flux to supply well
- Treatability test showed indigenous sulfolane degrading population
- Proximity to supply wells needs careful assessment of remediation needs/water quality effects

Oxygen sparging setup



GAC & On-Site Regeneration





- GAC does not have sorption capacity for sulfolane = excessive GAC consumption
- Countercurrent aeration to promote sulfolane degradation in the bed to restore GAC capacity
- Successfully restored 90% GAC capacity 4 times
- Can be applied in a batch setup to reduce waste disposal costs

Other Technologies

In situ aerobic bioremediation – Cold temperatures

- Nutrient limitation at high sulfolane concentrations
- Degradation @ ~ 12 ug/L/day – 2.9 mg/L/day; retarded in hydrocarbon co-contaminated system

Anaerobic Batch Tests

- Very slow kinetics (site/water chemistry specific)
- Thiolane generated as intermediate and inhibitory

Soil Washing + Advanced Oxidation Procedure (AOP) or ISCO

- Higher recovery/lower flush requirement for permeable soils
- UV/peroxide, ozone, alk ozone effective but oxidant demand driven by co-contaminants, scavengers

Phytoremediation

- Primarily tested in wetlands (cattails); Accumulates in foliage and some metabolism suspected
- Leaf/biomass decay may result in partial release
- Preferential over other similar co-contaminants (DIPA)

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KEY TAKEAWAYS

Key Takeaways

Sulfolane moves fast but can also disappear fast!!!

Key factors:

- Proper understanding of CSM
- GW flow = sulfolane migration (no retardation)
- Degradation kinetics and technology limitations

Recent technology development/path forward:

- Biomarkers; new microbial communities for colder temperatures
- Innovative adaptation of conventional technologies
- Passive/semi-passive technologies

Questions?

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