Safer Alternatives to Methanol in Windshield Washer Fluid

Greener Research Materials Symposium

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Outline

1. **Background**
   - Methanol use in windshield washer fluids
   - Environmental impact

2. **Freezing Point Depression**
   - Proposed chemicals
   - Safety data
   - Experiments
   - Preliminary results

3. **Microemulsion Systems**
   - What is a microemulsion?
   - Factors affecting systems
   - Planned experimental approach

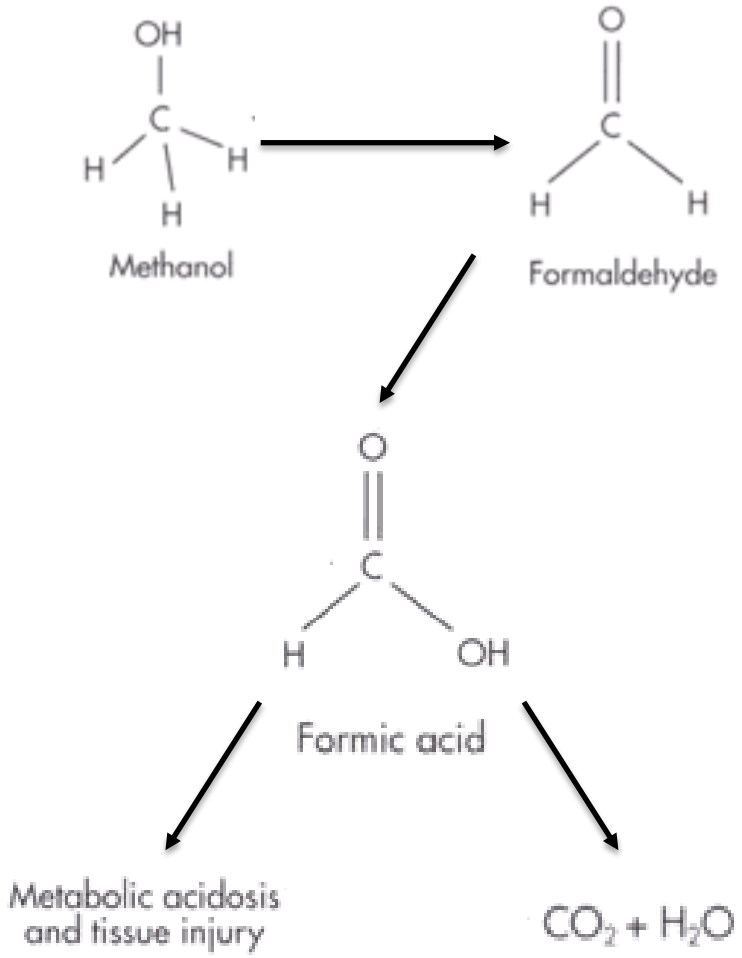
Background/Problem

Methanol → evaporates readily, excellent antifreeze and cleaner but is toxic

- Toxic effects in high vapor concentration, absorption through skin, and/or ingestion
- Initial effects: drowsiness, CNS depression, nausea, vomiting, confusion, headache, ataxia
- Repeated exposure: inflammation of eye, headaches, giddiness, insomnia, stomach disturbances, visual failure, skin irritation

Methanol use in Massachusetts

- Approximately 57 million pounds (2013)
- Majority of methanol used for windshield washer fluid products

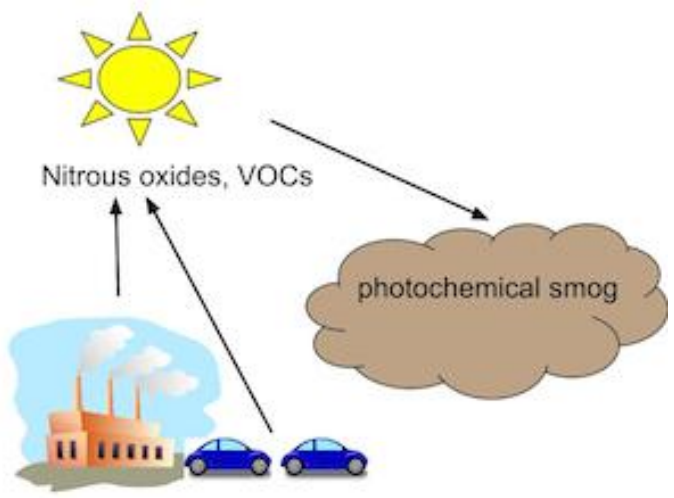


https://www.cdc.gov/niosh/ershdb/emergencyresponsecard_29750029.html

Background/Problem

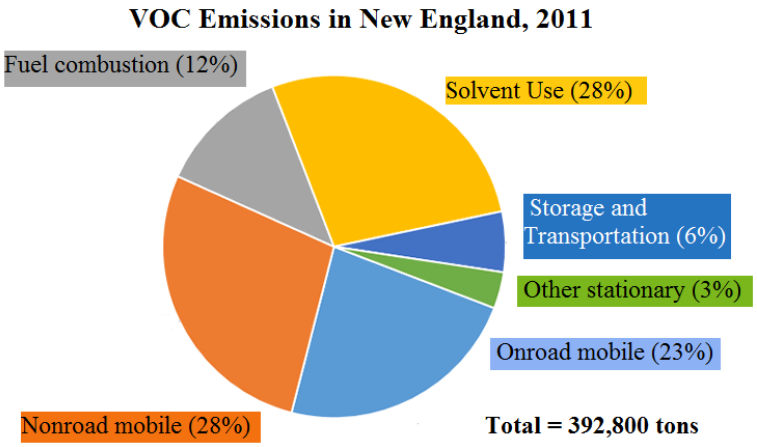
Volatile organic compounds (VOCs) cause considerable impact to the environment

- Volatile compounds of carbon that participates in photochemical reactions in atmosphere
- Methanol is a VOC



392,800 tons of VOC's emitted in New England in 2011

- >29,500 tons/yr of methanol in MA (2011)



http://www.mass.gov/eea/docs/dep/toxics/tura/11relfin.pdf

Goals

Mission Statement: We want to develop an environmentally friendly windshield washer fluid with a suitable freezing point and competitive price.

Develop windshield washer formulation with reduced VOC/methanol

- <35 wt% methanol
- Less harmful than current formulations

Reduce cost of formulation to compete with existing formulations

- ~$0.90/gal when >100,000 gallons produced

Maintain formula with low freezing point

- Freezes at/below -29°C (-20°F)

Conserve/enhance cleaning properties

- Clean polar and nonpolar substances
- Maintain windshield visibility

Ensure formulation is stable in various conditions

- Temperature
- Humidity
- Salinity

Retain formulation compatibility with vehicle equipment

- Wiper blades
- Tubing
- Paint
- Metal

Determining Freezing Point Depression Chemicals

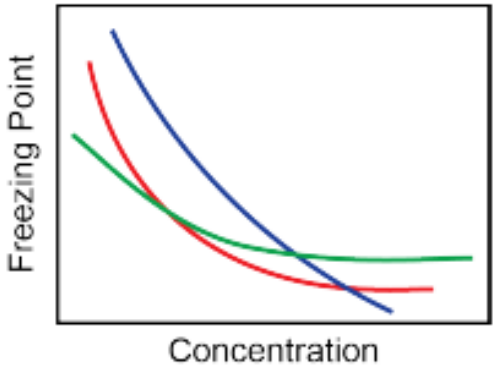
Propose freezing point depression chemicals

HSP software and literature values to investigate limits of solubility

Preliminary testing of freezing point formulations
-4→-20→-10 or -30 °F

Investigate synergistic effects of freezing point depression

Choose candidate systems to proceed to surfactant/ microemulsion systems



Chemical Hazard Awareness

- Chemicals listed have potential to be harmful/fatal in case of ingestion
- Permissible exposure limits (PEL) based on OSHA and NIOSH
- Methanol considered dangerous in case of percutaneous absorption

Chemical	PEL (mg/m^3)	MSDS Health Rating	MA TURA List	Pharos
Methanol	260	2	Yes	Red
Solvent 1	1900	1	No	Red (cancer)
Solvent 2	360	1	No	Orange
Solvent 3	980	2	Yes	Orange
Solvent 4	300	1	Yes	Orange
Solvent 5	3100	2	No	Orange
Solvent 6	500	1	No	Orange
Solvent 7	300	2	Yes	Orange
Solvent 8	610	1	Yes	Orange
Solvent 9	N/A	2	No	Grey
Solvent 10	15	1	No	Orange

https://www.osha.gov/dsg/annotated-pels/

http://onlinelibrary.wiley.com/book/10.1002/9783527682027

Freezing Point Depression Experiments

Phase 1: Investigate component X's freezing point depression capabilities

Objective: Determine component X's ability to lower freezing point in place methanol

Constant: 60 wt% water

Independent Variable: wt% methanol displaced by chemical X (see Table 1)

Target: 5-7 Chemicals capable of suitable freezing point depression

Table 1: Phase 1 Solutions

Solution	Methanol (wt%)	X (wt%)
1	30	10
2	20	20
3	10	30
4	0	40

Phase 2: Investigate freezing point depression of two components in mixture

Objective: Determine components X and Y's collective ability to lower freezing point in place of methanol

Constant: 60 wt% water

Independent Variable: wt% methanol displaced by chemical X and Y (see Table 2)

Target: 4-6 Potential freezing point formulations for microemulsion systems

Table 2: Phase 2 Solutions

Solution	Methanol (wt%)	X (wt%)	Y (wt%)
1	20	10	10
2	0	20	20

Preliminary Results

Phase 2 screening results:

Table 1: Preliminary freezing point data for polar substances

Chemical Mixture	10-10 wt%	20-20 wt%
Solvent 1 - Solvent 2	✓	O
Solvent 1 - Solvent 3	✓	✓
Solvent 1 - Solvent 4	O	O
Solvent 1 - Solvent 5	O	X
Solvent 1 - Solvent 6	O	O
Solvent 2 - Solvent 3	✓	✓
Solvent 2 - Solvent 4	O	O
Solvent 2 - Solvent 5	O	O
Solvent 2 - Solvent 6	O	O
Solvent 3 - Solvent 4	✓	X
Solvent 3 - Solvent 5	✓	O
Solvent 3 - Solvent 6	O	O
Solvent 3 - Solvent 7	✓	X
Solvent 3 - Solvent 8	✓	O
Solvent 4 - Solvent 5	O	X
Solvent 4 - Solvent 6	X	X
Solvent 5 - Solvent 6	O	X

KEY

✓ → liquid at -20°F
O → liquid at -10°F
X → solid at -10°F

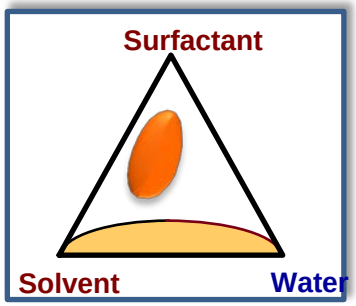
Experimental Info

- 45 minute trials
- Run in triplicate
- 10% X, 10% Y, 20% methanol, 60% water
- 20% X, 20% Y, 60% water

Formulating Microemulsions

Starting Point:
Low Freezing Point Fluid

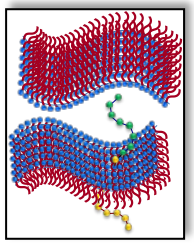
Microemulsion
- **Surfactant**
- **Oil**



Microemulsion System to Boost Cleaning

- Ultralow Interfacial Tension
- Spontaneous Formation
- Hydrophilic & Hydrophobic Soils
- Single Phase Appearance
- Thermodynamic Stability

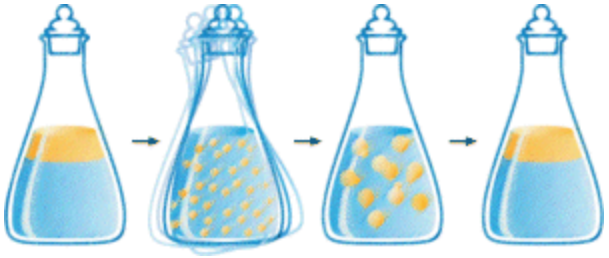
Pre-Microemulsion Surfactant Package for In-Situ Microemulsion



Microemulsions

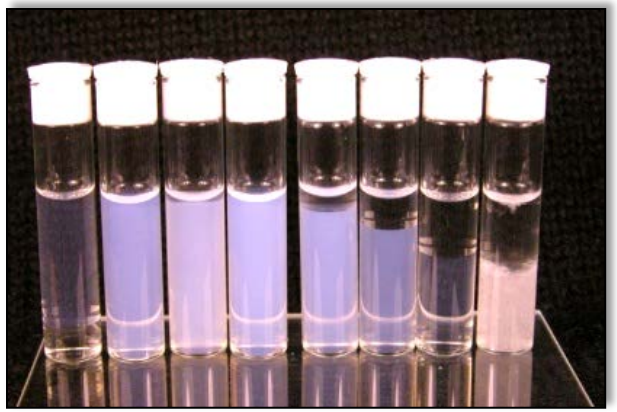
What is a microemulsion?

- Dispersion of two ordinarily immiscible fluids stabilized by an amphiphile/surfactant



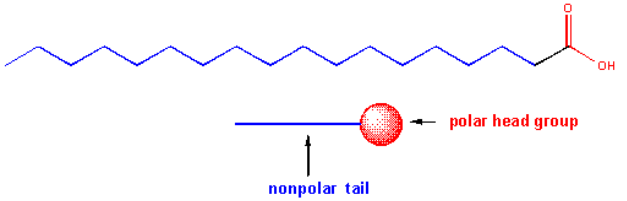
What makes them so good?

- Hydrophilic and lipophilic phases
- Large interfacial area → improved cleaner contact
- Tunable properties
- Can have high surfactant efficiency → reduced cost



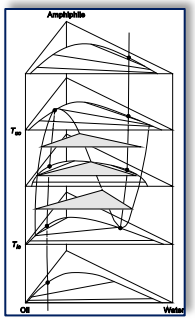
Where are they used?

- Industrial/consumer cleaners
- Catalysis
- Oil recovery
- Cosmetics and pharmaceuticals
- Foods



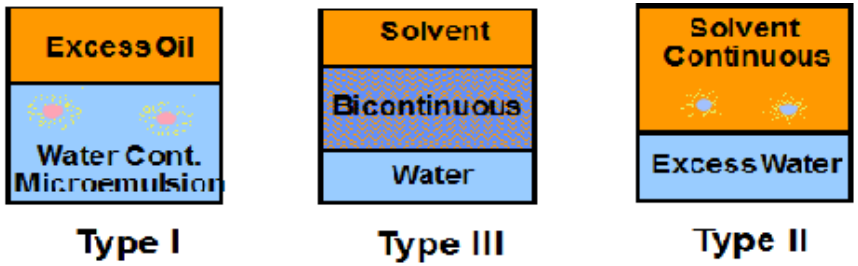
Factors of Microemulsion System

Ionic charge
- Nonionic vs ionic (cat., an., zwitt.)



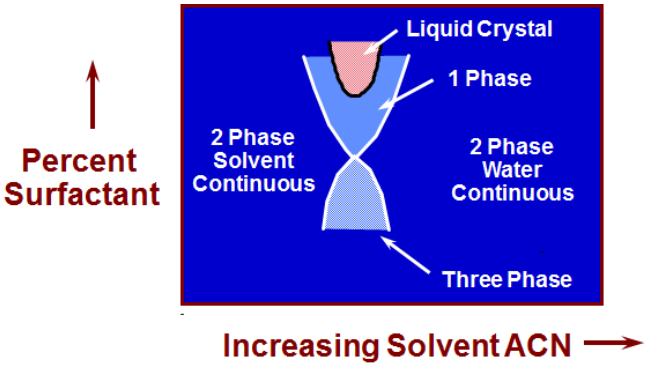
pH
- Important for charged surfactants
- Anionics can be less polar in lower pH

Temperature
- Can make more oil/water continuous



Salinity
- Salt ions screen polar group interactions
- More salt, more oil continuous

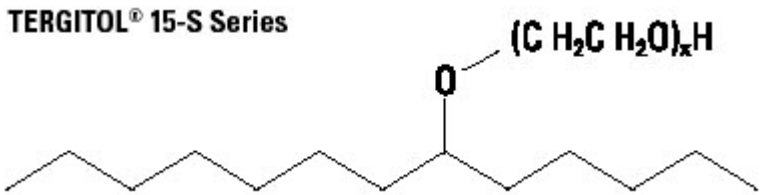
Solvent/Surfactant System
- Solvent alkane carbon number (ACN) → higher ACN, more water continuous
- Functional groups of surfactant
- Hydrophilic/lipophilic (HLB) balance



Proposed Surfactants for HLB Investigation

Tergitol15-S surfactant series

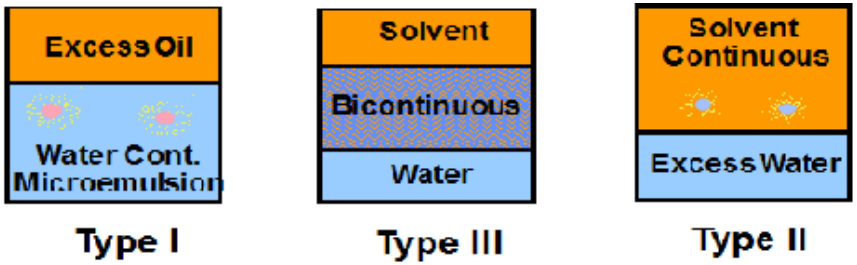
- 15-S-3 (HLB: 8.0)
- 15-S-9 (HLB: 13.3)
- 15-S-30 (HLB: 17.4)

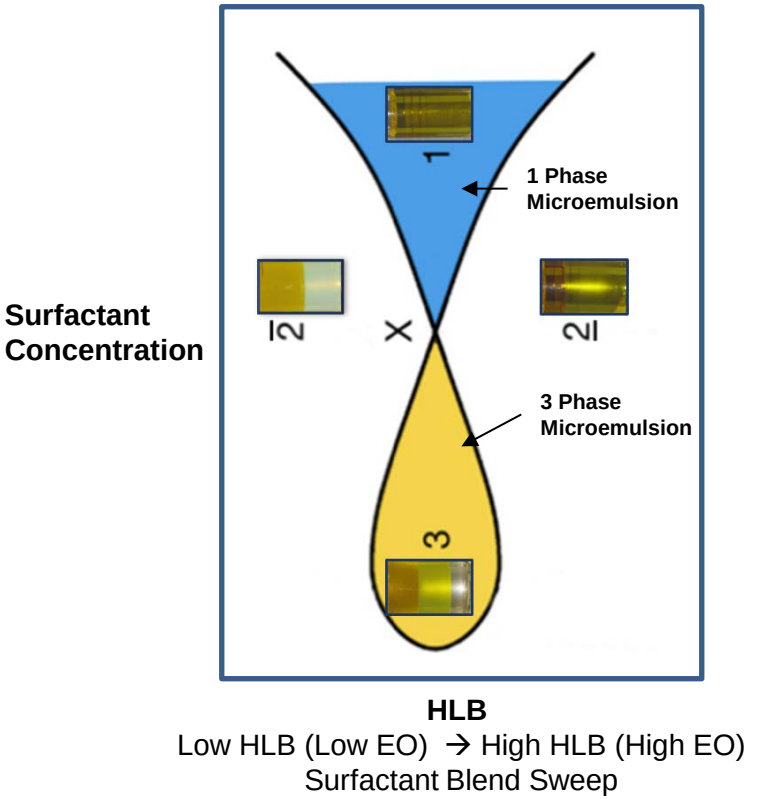


General Structure

- Secondary alcohol ethoxylate
- $C_{12\text{-}14}H_{25\text{-}29}O[CH_2CH_2O]_xH$

Purpose: Use these surfactants as a gauge for optimal HLB





Surfactant Experiments

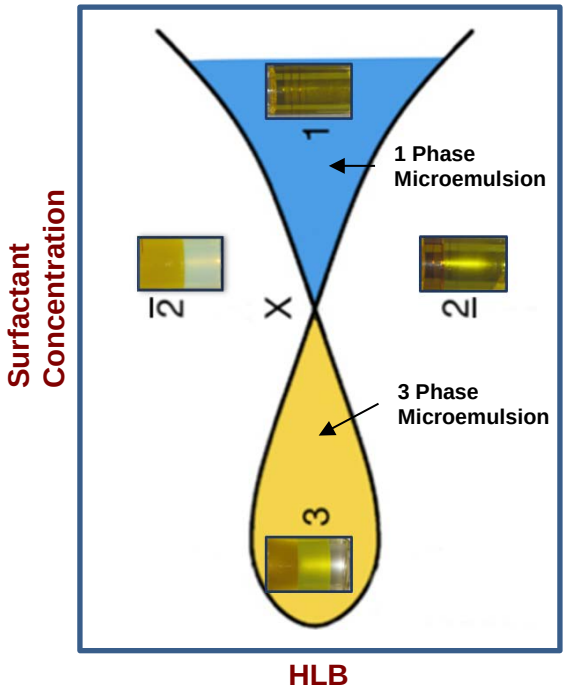
Phase 1: Investigate surfactant X's solubilizing capabilities

Objective: Determine surfactant X's ability to dissolve a given amount of D-limonene

Constants: 250mg formulation, 25mg D-limonene

Independent Variable: amount of surfactant X

Target: Gain insight into desired HLB of surfactant



Phase 2: Investigate solubilizing capability of two surfactants in mixture

Objective: Determine surfactants' X and Y collective ability to dissolve a given amount of D-limonene

Constant: 250mg particular formulation, 25mg D-limonene

Independent Variable: amount of surfactant X and Y

Target: Determine optimal HLB of surfactant for desired performance

Table 2: Surfactant mixture compositions

Surfactant Mixture	X (wt%)	Y (wt%)
1	25	75
2	50	50
3	75	25

Summary

Goal: Reduce methanol (a toxic VOC) content in windshield washer fluid

- <35 wt% methanol
- Does not freeze below -20°F
- Relatively inexpensive
- Stable in various environments
- Maintains cleaning properties
- Compatible with existing automobile parts

Freezing Point Depression

- Identified candidate solvent systems for microemulsion

Microemulsion Systems

- Use microemulsion technology for cleaning properties and stability
- Identify optimal surfactant HLB for system

Acknowledgements

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- Funding
- Resources

THANK YOU

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