Identification and Study of Alternatives to Ozone Depleting Solvents

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Code: 6185

Haloalkanes

Commercial Solvents

- CFCs (Chlorofluorocarbons)
- HCFC (Hydrofluorocarbons)

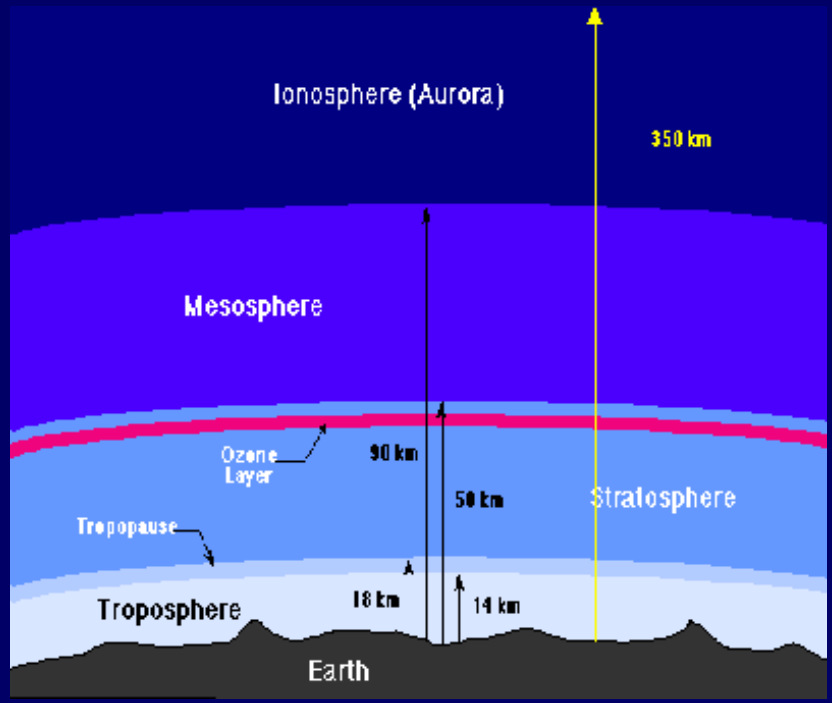
Environmental Effects

- Depletion of Ozone Layer
- Global Warming

CFCs------Chlorofluorocarbons

Ozone Depletion

- Lack of reactivity=Long Atmospheric Lifetime
- Diffuse into the stratosphere where CFCs are broken down by ultraviolet light and release chlorine atoms
- Chlorine Atoms Deplete the Ozone Layer
- Simple Mechanism:
  $Cl + O_3 \rightarrow ClO + O_2$
  $ClO + O \rightarrow Cl + O_2$



Contribution to Global Warming

- Strong IR absorbance contributed by the C-F bond results in High Global Warming Potentials

Aims of Project

- The purpose of this study is to find alternatives to replace CFC 113,HCFC 141b and HCFC 225 that do not deplete the ozone layer and do not have large Global Warming Potentials.

- Experimental Protocol:
  - (1) Contain Chlorine or Bromine
  - (2) Short atmospheric lifespan (1-4 weeks)
  - (3) Fluorine to Hydrogen ratio should be high enough so the compound is not flammable
  - (4) Compound should be non-toxic
  - (5) The compound should have a boiling point between 40 and 80 degrees Celsius.

Alkene and Ether Study: Approach

- Comparison of Kauri Butanol and Alkane Miscibility Limit values of tested Alkenes and Ethers to CFC 113, HCFC 141b, and HCFC 225

- Chemical Structure of Tested Compounds Studied in Correlation with K-B and AML values

Kauri Butanol Value

- The kauri-butanol value is used as a measure of the solvent power of hydrocarbon solvents

- K-B value: number of milliliters of test solvent to turn a certain number of grams of a standard solution of Kauri gum in n-butanol cloudy

Alkane Miscibility Limit (AML)

- Find the largest n-alkane that is soluble in the solvent being tested.
- The larger the n-alkane that is soluble in the solvent the more effective the solvent is.
- The AML was tested up to a n-alkane of C-22 for all of the tested solvents
- PROCEDURE:
  - 1 ml of solvent + 1 ml of n-alkane in vial
  - If miscible (no phase separation or cloudiness) continue to test n-alkanes of greater lengths until not miscible.

KB and AML Results

Solvent	KB Value	AML Value
CFCs&HCFCs TESTED		
CFC-113	32	20
HCFC-141b	54	20
HCFC-225 ca/cb	33	19
ALKENES TESTED		
1H, 1H, 2H-perfluoro-1-hexene	9	12
4-bromo, 3,3,4,4-tetrafluoro-1-butene	31	19
2-bromo, 3,3,4,4,4-pentafluoro-1-butene	27	19
2-bromo, 1,1,1,4,4,4-hexafluoro-2-butene	18	18
4-bromo, 3-chloro, 3,4,4-trifluoro-1-butene	84	20
2-chloro-3,4,4,4-trifluoro-3-trifluromethyl-1-butene	15	18
ETHERS TESTED		
2-Chloro-1,1,2-trifluoroethyl difluoromethyl ether	25	
2-Chloro-1,1,2-trifluoroethyl ethyl ether	33	
2-Chloro-1,1,2-trifuloroethyl methyl ether	31	
2-2-Dichloro-1,1-difluoroethyl methyl ether	60	
1,1-Dichloro-2,2,2-trifluoroethyl difluoromethyl ether	23	
Nonafluorobutyl methyl ether (HFE 7100)	9	9

Using Amphiphiles to Increase the Solvency of Non-chlorinated Solvents

- KB value of HFE 7100: 9
- AML for HFE 7100: 9

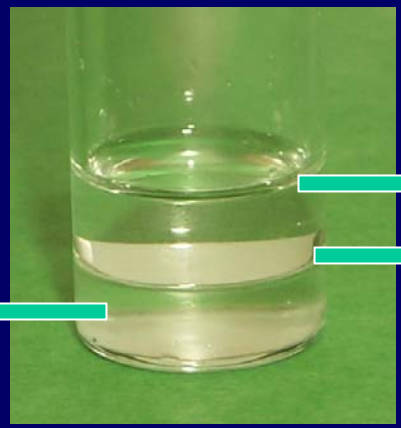
Indicate--HFE 7100 is not a very good solvent

- HFE 7100 properties: ODP=0; relatively low GWP
- Can addition of a fluorocarbon-hydrocarbon amphiphile make HFE 7100 a more effective solvent
- Fluorocarbon-hydrocarbon amphiphiles consist of one end that points toward the fluorocarbon concentrated area and one end that points toward the hydrocarbon concentrated area.
- Amphiphiles Used:
  - 1-Perfluoro-n-hexyl-dodecane
  - 1-Perfluoro-n-hexyl-tetradecane

Titration Study Using Amphiphiles to Increase the AMLs of HFE 7100-Procedure

- 1 ml of HFE 7100 and 1 ml of n-alkane
- Add amphiphile in 0.05 ml increments
- Shake after each increment is added
- Addition of increments continued until miscible

Titration Study Using Amphiphiles to Increase the AMLs of HFE 7100

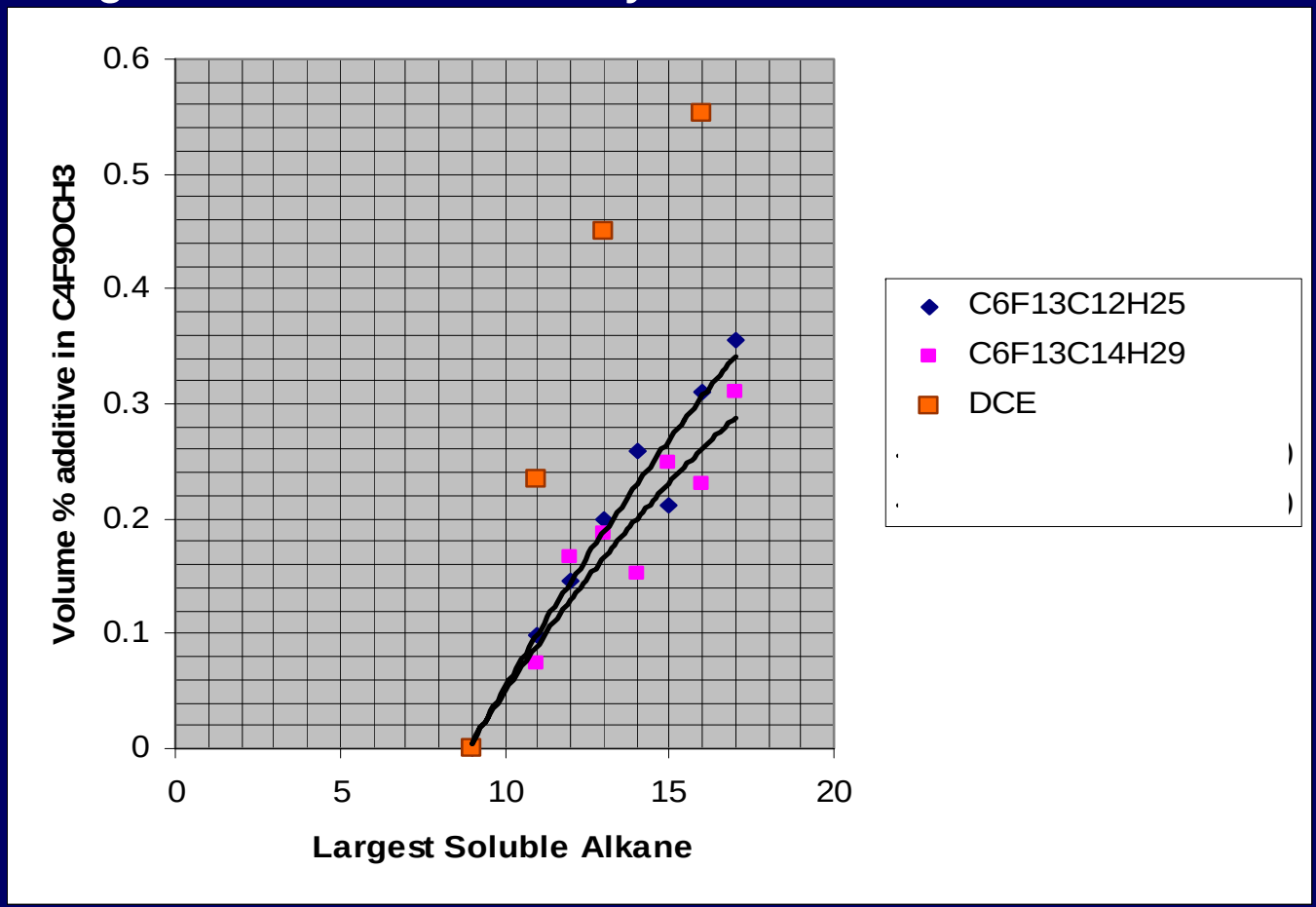


Amount of Amphiphile Added: 0.00 ml

0.05 ml 0.10 ml 0.15 ml 0.20 ml

Pictures Taken By Andy Awtry

Graph: Volume % additive in HFE 7100 versus the Largest Soluble Alkane—NRL HFE 7100 AML Data and 3M's AML Data Using trans 1,2-Dichloroethylene as the Additive



Discoveries

- 4-bromo, 3,3,4,4-tetrafluoro-1-butene Alkene was identified as a promising replacement solvent
- Fluorocarbon-hydrocarbon amphiphiles do increase the solvency properties of non-chlorinated solvents as shown with HFE 7100

Acknowledgements

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