

# The Effect of Ozonolysis on the Freezing of Water Catalyzed by High Molecular Weight Organic Compounds

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## Abstract

High altitude clouds may be impacted by the products of biomass burning which can be lofted into the upper troposphere through deep convection. Some high molecular weight organic compounds are efficient ice nucleators (e.g. long chain alcohols) while others are not (e.g. long chain alkanes). To further complicate the picture, once in the atmosphere organic compounds may be transformed through oxidation and photochemistry, which could change their characteristics as freezing catalysts. To develop a deeper understanding of these processes, we observed the freezing temperatures of pure water droplets covered by high molecular weight organic compounds before and after exposure to ozone. Oleic acid and oleyl alcohol, which have carbon-carbon double bonds at the same position along the backbone of the molecule, display very different behaviors. The mean freezing temperature for oleic acid is unchanged after exposure to ozone while that for oleyl alcohol increases by approximately 4 K. Octadecene shows no change in freezing efficacy upon exposure to  $O_3$ .

### High molecular weight organics on water

The compounds studied are virtually insoluble in water.

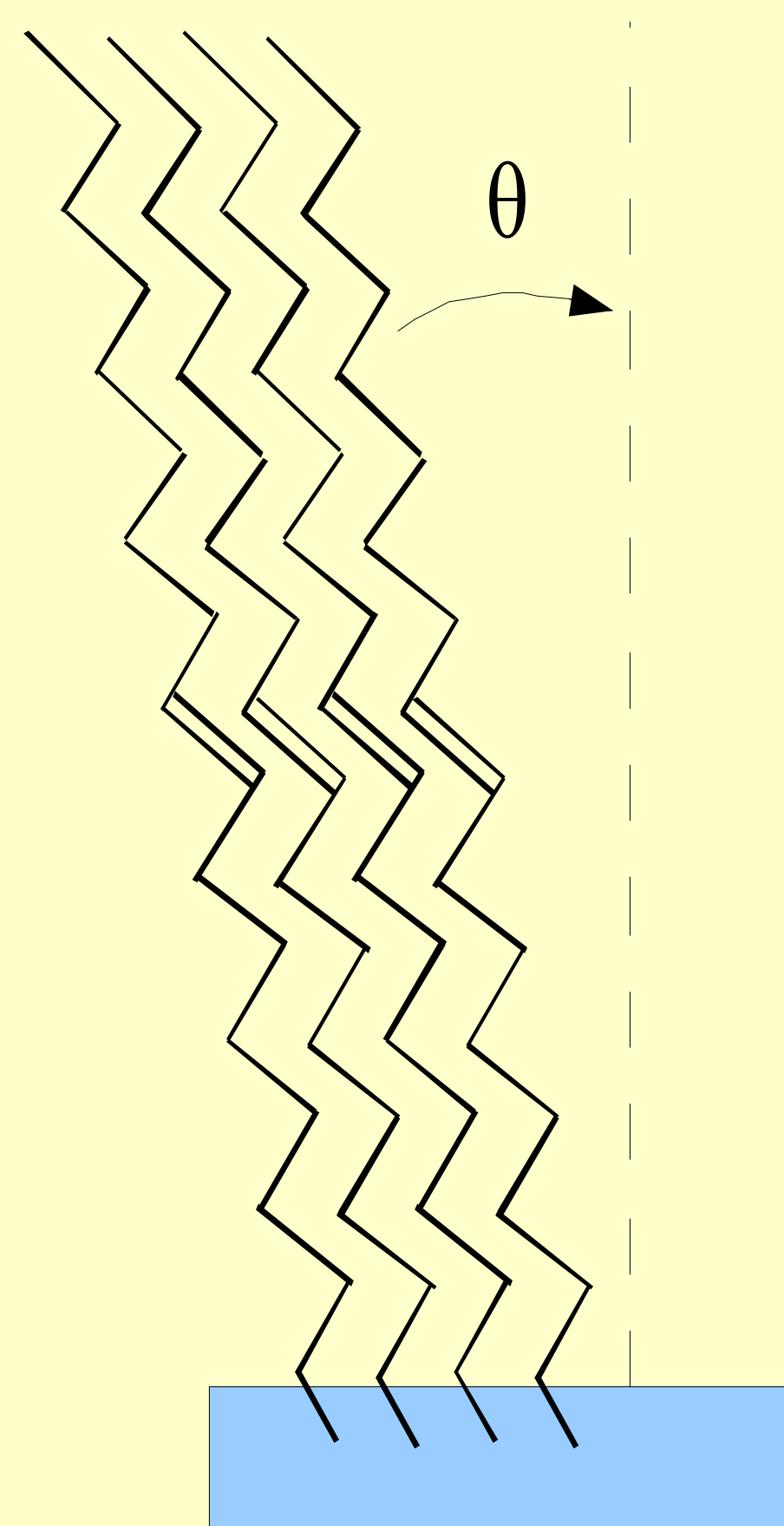
The polar compounds self assemble at the air-water interface into 2D crystals (for monolayer coverage) as shown in Figure 1.

### Reaction with $O_3$

$O_3$  + oleyl alcohol  $\rightarrow$  nonanal, nonanoic acid, 9-hydroxynonanal and 9-hydroxynonanoic acid (nonanal is volatile)

$O_3$  + oleic acid  $\rightarrow$  nonanal, nonanoic acid, 9-oxononanoic acid, azelaic acid, and 9-oxooctadecanoic acid (secondary product). (nonanal is volatile)

$O_3$  + 1-octadecene  $\rightarrow$  formic and heptadecanoic acid, formaldehyde, and heptadecanol. (formaldehyde is volatile) (Hearn and Smith, 2004)

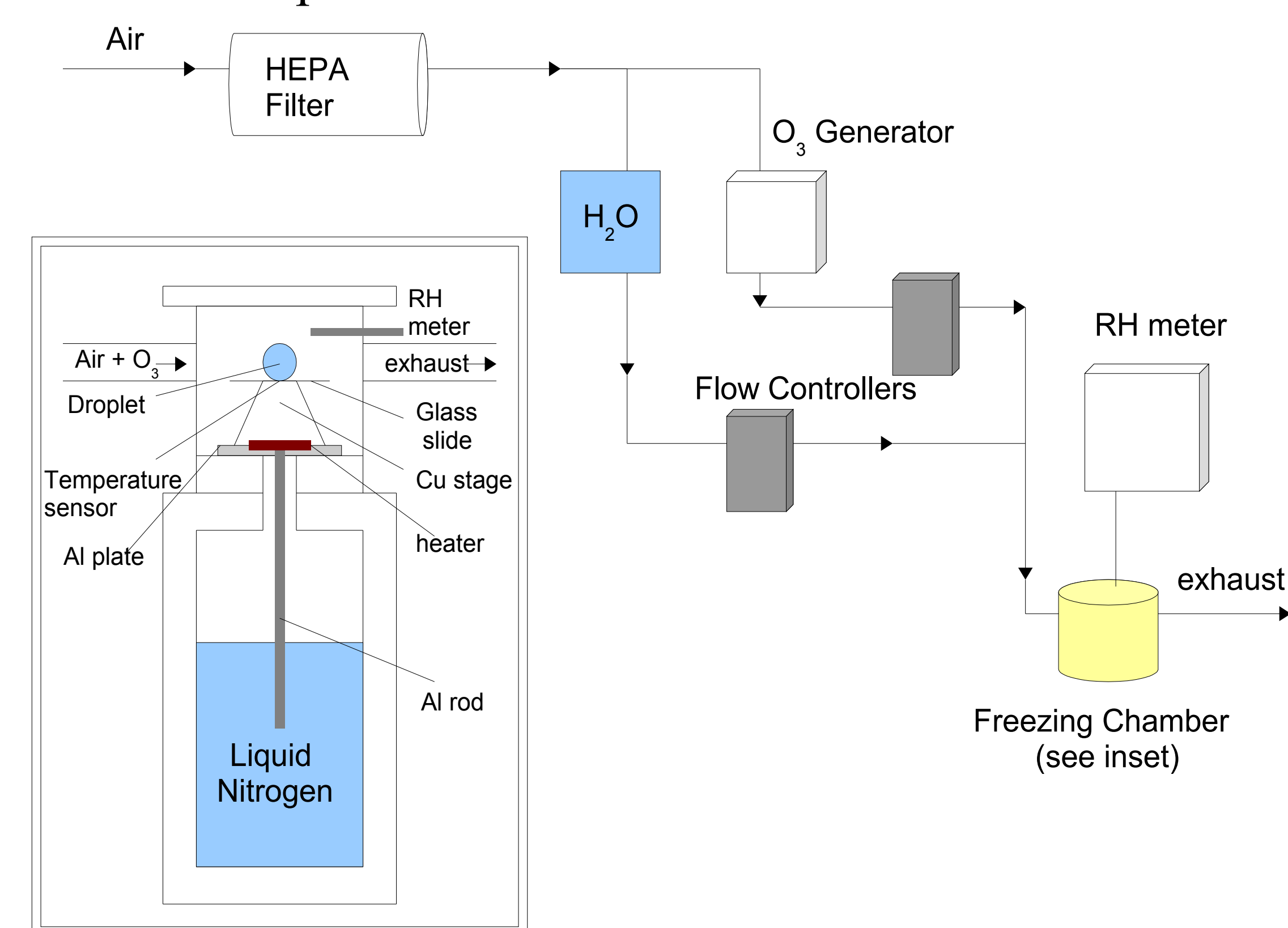


**Figure 1.** Schematic of a monolayer of an amphiphilic, insoluble organic on the surface of water.

## Experimental Details

### Procedure

- Freeze pure water droplet (5  $\mu$ l) 3-4 times to verify  $T_{freeze} < -24$  °C
- Deposit organic film on droplet (via chloroform spreading solution)
- Freeze droplet-film  $\sim 10$  times
- Expose droplet (unfrozen) to ozone for 0.25 to 5 hours (T constant, usually -10 °C).
- Freeze droplet  $\sim 10$  times



RH at the droplet is  $\sim 100\%$  to ensure it neither grows nor shrinks during the experiment.

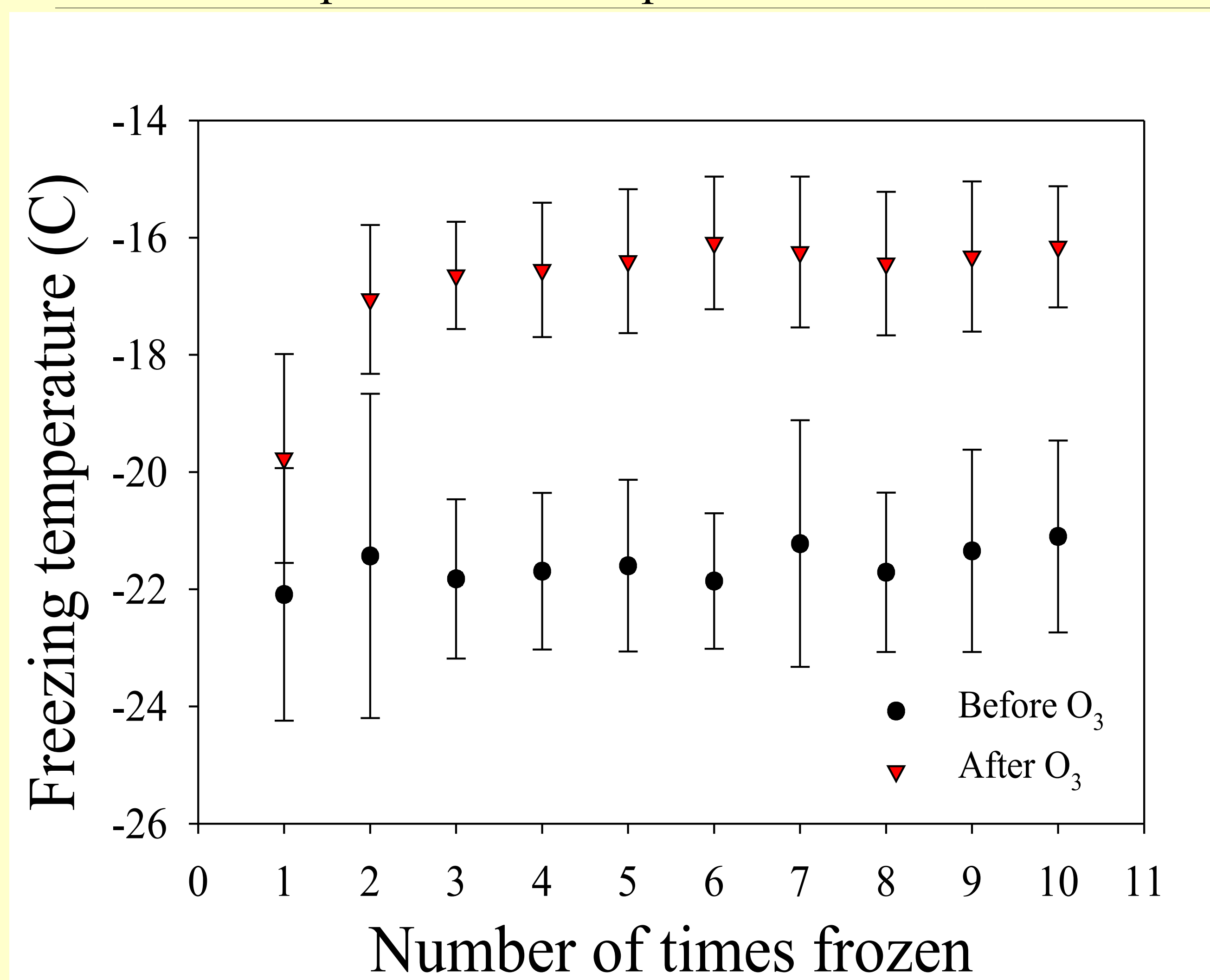
Concentration of  $O_3$  is  $\sim 0.5$  ppm

$-dT/dt = 2$  K/min  
 $+dT/dt = 4$  K/min

Droplet is warmed to 12 °C during thaw cycle (unless otherwise specified.)

Freezing of the droplet is detected from the presence of the latent heat pulse.

Compound	$T_{freeze}$ (before $O_3$ )	$T_{freeze}$ (after $O_3$ )	Notes
Oleyl alcohol cis- $CH_3(CH_2)_7CH=CH(CH_2)_7CH_2OH$ 2.5nmol deposited onto drop (multilayer film) (see Figure 2)	$-21 \pm 2$	$-17.0 \pm 1.4$	$C_{18}H_{37}OH$ (no double bond) catalyzes freezing at $\sim -11$ °C (Popovitz-Biro et al., 1994).
Oleic acid $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$ 2.5 nmol deposited onto drop	$-24.3 \pm 0.7$	$-24.2 \pm 0.7$	
1-octadecene $CH_2=CH(CH_2)_{15}CH_3$ 2.5 nmol deposited onto drop	$-25 \pm 1.4$	$-25 \pm 1.5$	The melting point of 1-octadecene is 17 °C. No difference in trials where $T_{max} < T_{melt}$ and $T_{max} > T_{melt}$ .
1-octadecene 500 nmol deposited onto droplet	$-22 \pm 2$	$-22 \pm 2$	$T_{max} < T_{melt}$
1-octadecene 0.25 nmol deposited onto drop	$-25 \pm 1$	$-26 \pm 1$	$T_{max} < T_{melt}$



**Figure 2.** Freezing temperature of water catalyzed by oleyl alcohol before exposure to ozone and the resulting products after exposure. The increase of  $\sim 4$  K occurs primarily in the first two freezing cycles.

$$\tau_{Debye} = \frac{8\pi\eta a^3}{2kT} \quad \tau_{diffusion} = \frac{l^2}{2D}$$

$\eta$  = viscosity (4 centipoise)

$a$  = molecular dimension (20 Å)

$l$  = thickness of film (10 Å)

$D$  = self diffusion constant ( $0.5 \times 10^{10}$  Å<sup>2</sup>/s)

$k$  = Boltzmann's constant

Reorientation time is  $\sim 0.1$   $\mu$ sec

Diffusion time  $\sim 0.01$   $\mu$ sec

## Conclusions

- Cleaving the double bond in a film of oleyl alcohol alters the structure of the film, increasing  $T_{freeze}$
- Cleaving the double bond in a film of oleic acid has no effect on  $T_{freeze}$ . (Presumably the structure of the film changes, but not favorable to ice nucleation.)
- Environmental conditions (e.g. whether temperature rises above  $T_{melt, alkene}$ ) during and after exposure to  $O_3$  may be controlling factors in effect that films of long chain alkenes have on ice nucleation.

### References:

J. Hearn and G. Smith, *J. Phys. Chem A*, **2004**, 108, 10019-10029.  
Popovitz-Biro et al., *J. Am. Chem. Soc.*, **1994**, 116, 1179-1191.

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### Why is there a 4 K jump in $T_{freeze}$ after oleyl alcohol is exposed to $O_3$ , but not for oleic acid?

Oleyl alcohol and oleic acid differ only in their head groups. (Carbon-carbon double bond is in the same position along the chain.)

Cleaving the double bond in the alcohol allows structural rearrangement of the film to a better match with ice. (The acid headgroup provides a poor match for ice lattice regardless of the backbone.)

### Why is there no change in $T_{freeze}$ after exposing octadecene to $O_3$ ?

Polar headgroups created upon ozonolysis should interact with water more strongly.

1. Temperature during ozonolysis  $< T_{melt, octadecene}$  and  $T_{max}$  during subsequent freezing cycles  $< T_{melt, octadecene}$

The organic film is frozen during ozonolysis – only top layer reacts. Reacted products never in contact with water.

2. Temperature during ozonolysis  $< T_{melt, octadecene}$  and  $T_{max}$  during subsequent freezing cycles  $> T_{melt, octadecene}$

The organic film is frozen during ozonolysis – only top layer reacts. Reacted products (i.e. compounds with polar head groups) must re-orient toward water and/or diffuse through organic film to water interface.

Reorientation time and diffusion time are small compared to time spent at  $T > T_{melt}$ .

Organic compound must react, reorient, and form a domain large enough to serve as a nucleation site. Possible that not enough octadecene reacted to aggregate into domains at the water interface.