Ice Nucleation by Long Chain Alcohols: Perspectives on Nucleation Theories and the Structure of Water

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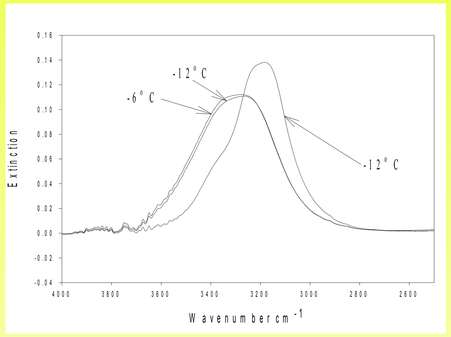
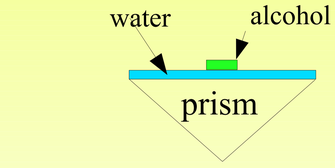
Our Motivation

Since the 1940s, a plethora of substances have been tested for their ability to promote ice nucleation. Though multiple theories trying to account for the results have risen over the years, the original one, the classical theory of heterogeneous nucleation, has remained as the most widely used. Unfortunately, this theory has in many cases been unsuccessful at explaining experimental results. In 1996, Gabor Vali summarized the uncertainties associated with ice nucleation with the comment: "the origins of ice particles are understood only partially and in very rough terms", and generally speaking, it is this understanding of ice formation that we hope to improve upon.

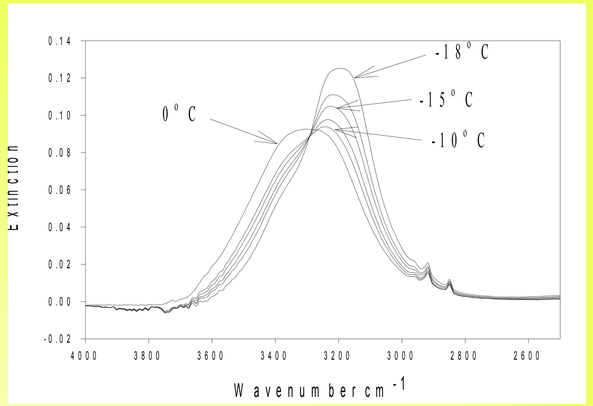
Heterogeneous ice nucleation mediated by long chain alcohols is particularly puzzling. Multiple,conflicting theories have been proposed to explain the freezing process as mediated by these alcohols [1,2,3,4]. In an attempt to resolve the conflict just mentioned, and more generally, to point towards a fundamentally sound theory, we have spectroscopically probed water films in contact with long chain alcohols as the systems are cooled through freezing transitions.

Spectral Results

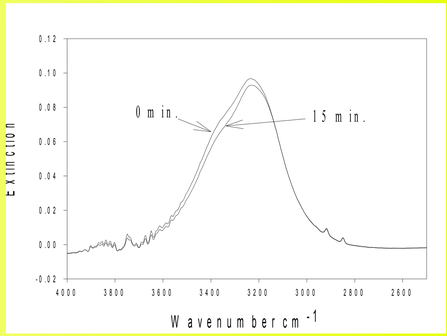


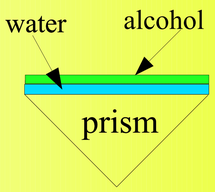


* partial alcohol coverage, cooled at-0.5° C/min
* subsequent freezing at ~ -12° C



*full alcohol coverage, cooled at -0.5° C/min
*no distinct freezing point
*quasi-isosbestic point observed





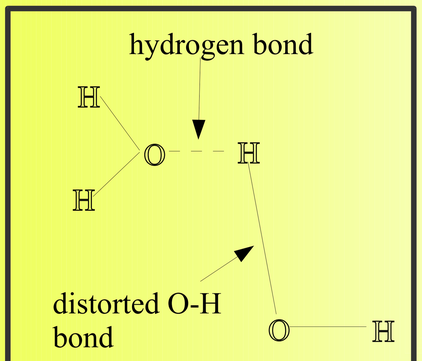
* full alcohol coverage, temperature held steady at ~ -11° C
* spectra remain nearly constant, yet resemble neither ice nor liquid water

The Experiment

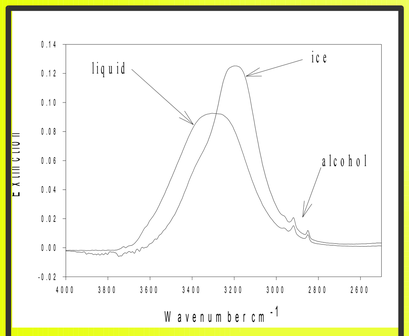
*spectra are taken every 30 sec while films are cooled

*obtained spectra are compared with the known spectral signatures of pure liquid and pure ice

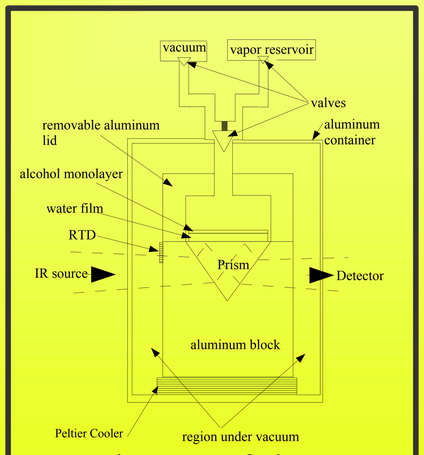
*information about the intermolecular environment that accompanies a freezing transition is inferred



A schematic of two water molecules interacting.

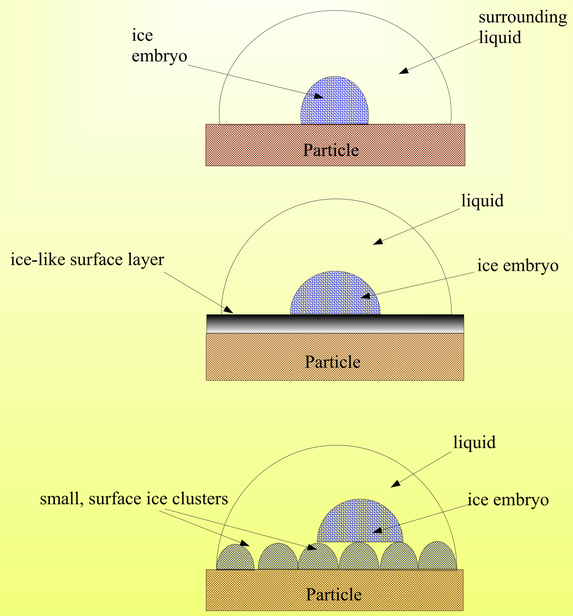


Spectra of liquid water (0° C) and ice (-18° C), covered with alcohols



A schematic of the experiment

Interpretations and Hypothesis



Schematics of previously proposed nucleation mechanisms [1, 3, 4]

Which of these pictures, if any, could explain our results?

* The full coverage of alcohol seems to promote a tendency towards freezing, yet by the same token, inhibits the formation of a critical nucleus (i.e. we never see a distinct freezing point).

* The isosbestic point in the spectra is consistent with a changing equilibrium ratio between strongly and weakly hydrogen bonded water molecules [5]

* Though the water filmpartially covered with an alcohol layer does exhibit a distinct freezing point, we suggest that even here, the precursors to nucleation could involve the existence of stable states of the water which resemble neither ice nor liquid

* A density functional approach could be our best bet for an understanding of this freezing process [2]

References

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Acknowledgments

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