

An Insight into the Ice Nucleation Process via Design of Crystalline Ice Nucleators of Variable Size

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Monolayers of the long-chain alcohols on water promote nucleation of ice. In order to determine the minimum size of crystalline alcohol monolayer domains that induce ice nucleation, we reduced their size in two distinct ways. One approach encompassed embedding the pure hydrocarbon alcohol, $C_nH_{2n+1}OH$ ($n = 20, 31$), into a matrix of an immiscible monolayer of perfluoro alcohol $C_{10}F_{21}C_2H_4OH$, which is inert as an ice nucleator. The second set of experiments involved the introduction of random defects into the monolayer crystalline domains of $C_{29}H_{59}OH$ through the use of the fully miscible guest alcohol molecule, $C_{31}H_{63}OH$, as additive. By these methods we estimated that ~ 450 water molecules are necessary to form a stable ice cluster at the onset of induced ice nucleation at a temperature just below 0°C .

The induced nucleation of ice by structured interfaces occurs in systems as diverse as frost bacteria^{1–3} and silver iodide in clouds seeded for the promotion of rain.⁴ Molecular dynamic simulations⁵ and nonlinear optical methods⁶ had been applied to study the interactions between structured surfaces and the organization of the water molecules at the interface. Here we describe experiments to glean information of the minimum size of an amphiphilic monolayer template needed to induce nucleation of ice.

Recently we demonstrated that crystalline monolayers in the amphiphilic alcohol series $C_nH_{2n+1}OH$ ($n = 13–31$), particularly for n odd and >23 , are very efficient ice nucleators of supercooled water drops, due to an epitaxial match between the monolayer 2-D crystal structure and the ab layer of hexagonal ice.^{7–9} Grazing incidence X-ray diffraction (GID) measurements using synchrotron radiation yielded a surprisingly low average coherence length of ~ 25 Å, parallel to the ab plane, of ice crystals nucleated by the $C_{31}H_{63}OH$ (abbreviated $C_{31}OH$) monolayer, when cooled at a very slow rate.¹⁰ This result was rationalized in terms of neighboring multinucleation ice centers separated at the monolayer interface by distances somewhat larger than 25 Å. Such length scales are in the same range as the size of, and separation between, neighboring lattice matching domains common to ice and the monolayer according to the Moiré fringe pattern arising from superposition of the two lattices (Figure 1). However, this observation is not inconsistent with large single ice crystals being nucleated by the monolayer, as was indeed demonstrated by X-ray powder diffraction measurements,⁸ and by electron microscopy,¹¹ which showed diffraction patterns from a micrometer-size ice single crystal and a $C_{31}OH$ crystalline monolayer in orientational registry. These various observations led to questions concerning the minimum size of the monolayer domains required to achieve efficient ice nucleation.

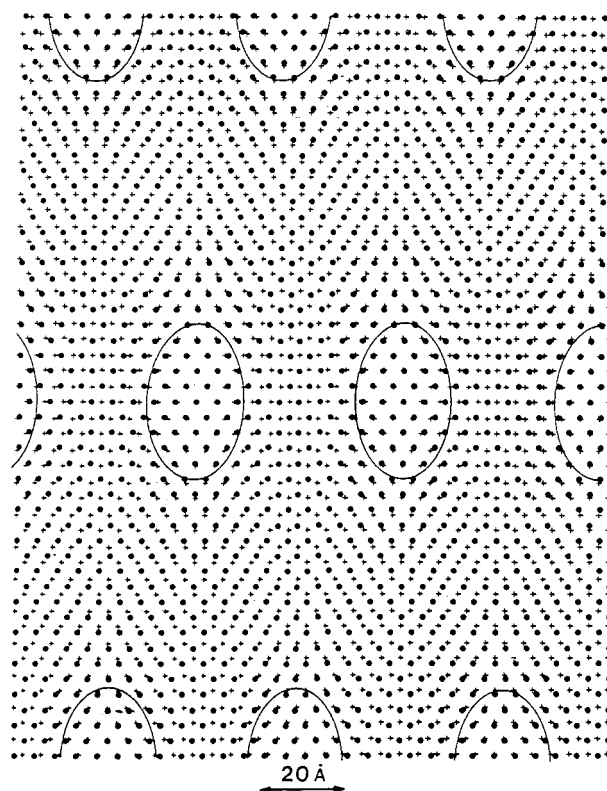


Figure 1. Moiré fringe pattern arising from a superposition of the ab lattices of the $C_{31}OH$ monolayer (circles) and ice (crosses). Elliptically shaped matching domains common to both lattices are delineated with an average diameter of 30 Å, within which the average distance between matched lattice points is 0.5 Å.

For the above purpose, experiments were designed to reduce the domain size of crystallites in two distinct ways. One approach encompassed embedding a pure hydrocarbon alcohol, C_nOH ($n = 20, 31$), in various molar ratios, into a matrix of an immiscible monolayer of perfluoro alcohol $C_{10}F_{21}C_2H_4OH$ (abbreviated $C_{12}F_{21}OH$),^{8,12} which is inert as an ice nucleator. The second set of experiments involved the introduction of random defects into the monolayer crystallite domains of $C_{29}OH$

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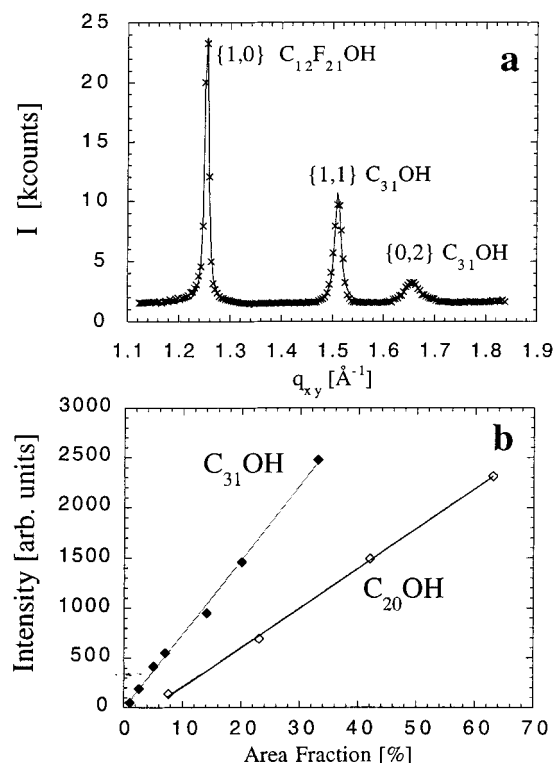


Figure 2. (a) Low-order Bragg peaks along the horizontal scattering vector q_{xy} from the (1:2) mixed monolayer of $C_{31}OH$ and $C_{10}F_{21}OH$, showing phase separation. The cell of the $C_{12}F_{21}OH$ monolayer is hexagonal so that the Miller h,k indices in $\{1,0\}$ represents the coinciding $(1,0)$, $(1,-1)$, $(0,1)$ and the corresponding $(-h,-k)$ reflections. The $C_{31}OH$ monolayer is rectangular, yielding the symmetry-related, and so coincident, $(1,1)$ and $(1,-1)$ peaks denoted as $\{1,1\}$, and the $\{0,2\}$ peak. (b) Integrated intensities of the $\{1,1\}$ Bragg peaks of the $C_{31}OH$ and $C_{20}OH$ monolayer as a function of their area fraction in the mixture with $C_{12}F_{21}OH$.

through the use of the slightly longer guest alcohol molecule, $C_{31}OH$, as additive, each amphiphile having an odd number of carbon atoms and so being an excellent ice nucleator in pure form. We aimed at a measure of the minimum average size of the hydrocarbon alcohol clusters, which would nucleate ice, by correlating the domain size of the nucleating alcohols with the temperature of ice formation from water drops covered by the corresponding mixtures.

First Approach: Fluorocarbon/Hydrocarbon Mixtures.

Here we use two different types of fluorocarbon/hydrocarbon alcohol mixtures, $C_{12}F_{21}OH/C_{20}OH$ and $C_{12}F_{21}OH/C_{31}OH$. The $C_{20}OH$ monolayer in pure form is a much poorer ice nucleator than $C_{31}OH$ for reasons already outlined elsewhere.⁸ GID measurements of the different monolayer mixtures on water at a temperature of 5 °C were performed on the liquid surface diffractometer at beam line BW1 at HASYLAB.¹³ The mixtures after deposition onto the water surface separated into two pure crystalline phases for all relative concentrations, as shown by their diffraction patterns. One such pattern obtained for the 2:1 $C_{12}F_{21}OH/C_{31}OH$ mixture is shown in Figure 2a.

The fluorocarbon chains pack in a hexagonal unit cell $a_H = 5.79$ Å with molecules aligned normal to the water surface. The hydrocarbon alcohol molecules pack in a rectangular unit cell, $a = 5.0$ Å and $b = 7.6$ Å for $C_{31}OH$, and $a = 5.0$ Å and $b = 8.1$ Å for $C_{20}OH$, each arranged in a herringbone structure⁹ via plane symmetry $p1g1$. The molecules of $C_{31}OH$ and $C_{20}OH$ are tilted in the direction of the b axis by approximately 12 and 19°, respectively, independent of mixture composition with the fluorocarbon alcohol.¹⁴ The linear relation between the integrated intensities of the Bragg peaks of C_nOH , $n = 31, 20$, and

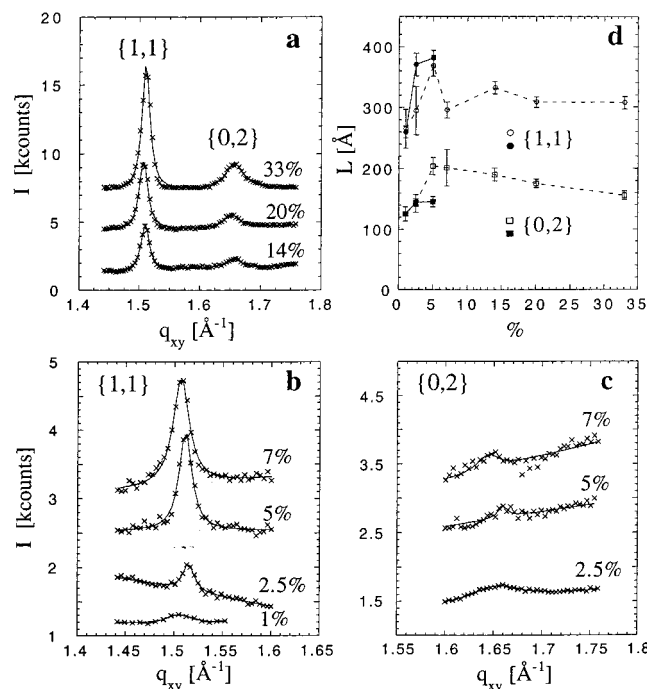


Figure 3. (a–c) The $\{1,1\}$ and $\{0,2\}$ Bragg peaks of the $C_{31}OH$ monolayer as a function of percent concentration in the mixture with $C_{12}F_{21}OH$. For clarity, the peaks have been offset along the vertical axis. (d) Crystalline coherence length along the $\{1,1\}$ and $\{0,2\}$ crystallographic directions of the $C_{31}OH$ monolayer as a function of concentration in the $C_{12}F_{21}OH/C_{31}OH$ mixture. Open and filled symbols represent two different series of experiments, respectively.

their area fraction in the $C_{12}F_{21}OH/C_nOH$ mixture (Figure 2b) indicates that the same relative percentage of the C_nOH component crystallizes in all compositions of the $C_{12}F_{21}OH/C_nOH$ mixtures. The remarkable result was that we have observed diffraction from the $C_{31}OH$ crystallites for as little as 1% in the $C_{12}F_{21}OH/C_{31}OH$ mixture (Figure 3b). The coherence lengths of the $C_{31}OH$ crystallites (Figure 3d), obtained by diffraction peak analysis,¹⁵ were anisotropic and almost constant for each reflection, extending approximately 300–370 Å in the $\{1,1\}$ and 180–200 Å in the $\{0,2\}$ crystallographic directions for concentrations of $\geq 5\%$. Only when the concentration of amphiphile $C_{31}OH$ dropped to 2.5 and 1% was a sharp decrease in coherence length observed. The coherence lengths for 1% concentration were as low as 120 Å in the $\{0,2\}$ direction and decreased to 260 Å along the $\{1,1\}$ direction. The coherence lengths of the $C_{20}OH$ crystallites, not shown, were also anisotropic and constant over the 10–100% concentration range examined, 480 Å in the $\{1,1\}$ and 250 Å in the $\{0,2\}$ directions.

The results of ice nucleation experiments performed on drops¹⁶ of H_2O or D_2O covered by monolayers of the above mixtures are shown in Figure 4. The two freezing curves have similar shapes, with a constant difference of ~ 2.5 °C as expected. When the relative concentration of the amphiphile $C_{20}OH$ in the $C_{12}F_{21}OH/C_{20}OH$ mixture falls below 50%, the freezing temperature of water begins to drop in a linear way (Figure 4a). On the other hand, there is a constant shallow decline in ice nucleation temperature with the decrease in concentration of $C_{31}OH$ in the $C_{12}F_{21}OH/C_{31}OH$ mixture from 100 to 5% (Figure 4b). The nucleation efficiency of $C_{31}OH$ for concentrations in the range from 100 to 5% is proportional to the number of nucleating domains, since the number of $C_{31}OH$ crystalline islands, whose coherence lengths remain by and large constant, falls off monotonically with concentration (vide supra). We arrive at a similar conclusion for $C_{20}OH$ except that the nucleation temperature only begins to go down

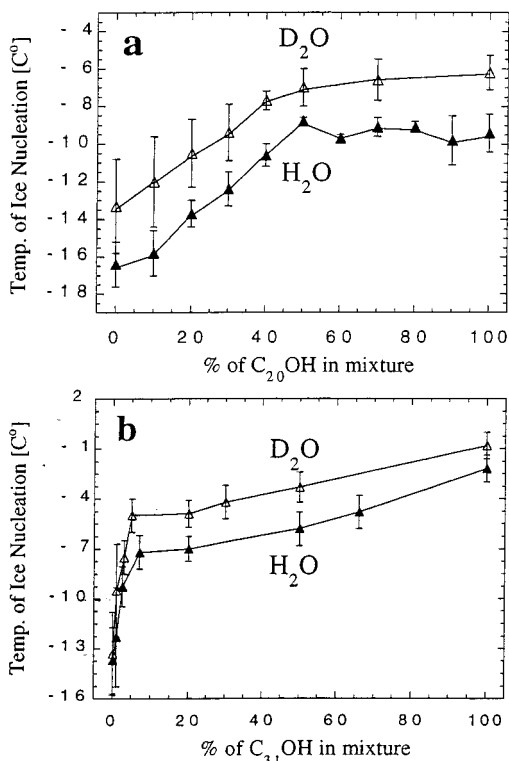


Figure 4. Freezing temperatures of supercooled drops of D₂O (Δ) and of H₂O (\blacktriangle) covered by mixed monolayers of (a) C₁₂F₂₁OH/C₂₀OH and (b) C₁₂F₂₁OH/C₃₁OH as a function of C₃₁OH percentage in the mixture.

when the number of C₂₀OH monolayer domains drops below a threshold value corresponding to a relative concentration of about 50%.

In the lower concentration regime of C₃₁OH (<5%), there is a steep fall in the temperature of nucleation which may, perhaps, be associated with the shorter coherence lengths of the C₃₁OH islands embedded in the sea of C₁₂F₂₁OH crystallites. This freezing curve is in keeping with theoretical prediction involving the dependence of minimal supercooling temperature of a bulk liquid phase on the domain size of the crystal nucleating template.¹⁷ The average size of 120 Å in the *b* direction of the C₃₁OH domains, for which the ice nucleation temperature dropped sharply, is decidedly larger than the coherence length of 25 Å in the *ab* plane of the ice crystals nucleated by the monolayer, as had been determined by GID.¹⁰

Second Approach: Hydrocarbon Mixtures of Different Lengths. Here we attempted to obtain ice-nucleating monolayer domains much smaller than 120 Å by introducing random defects into the monolayer crystallites. The curve of freezing temperature of water vs composition of the mixture of the two amphiphiles, C₂₉OH and C₃₁OH (Figure 5a), shows that C₃₁OH is a better contaminant than C₂₉OH, which we explain as follows. Lattice energy calculations¹⁸ involving the random introduction of guest C₃₁OH into a monolayer crystal of C₂₉OH, and vice versa, where the interaction between the monolayer and the water subphase was neglected, yielded three minimum energy arrangements,¹⁹ A, B, C, for each of the two possibilities, shown in Chart 1. Arrangement A is the most favorable, and B and C are almost equienergetic. Arrangement C in both a and b of Chart 1 has a smooth ordered OH surface, and thus should have no detrimental effect on the ice freezing temperature. The hydroxyl surfaces of arrangements A and B expose similar types of defects in both a and b of Chart 1. The defect sites in Chart 1a should be more disruptive toward formation of an ordered assembly of water molecules at the monolayer interface than the defects in Chart 1b, which is compatible with

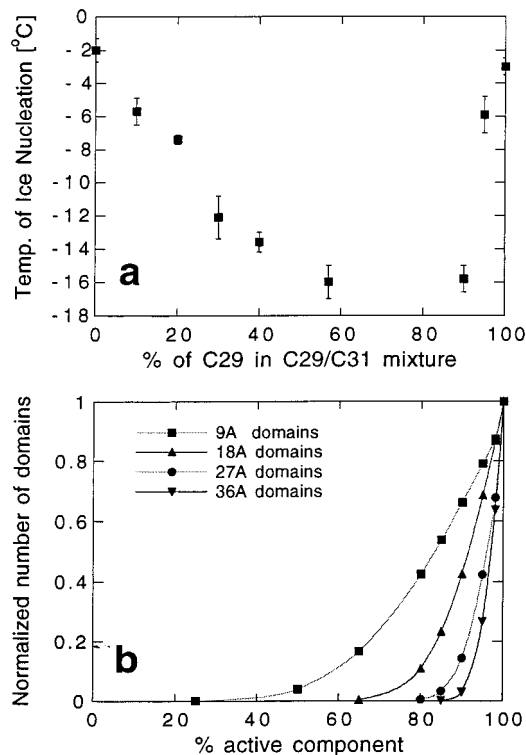
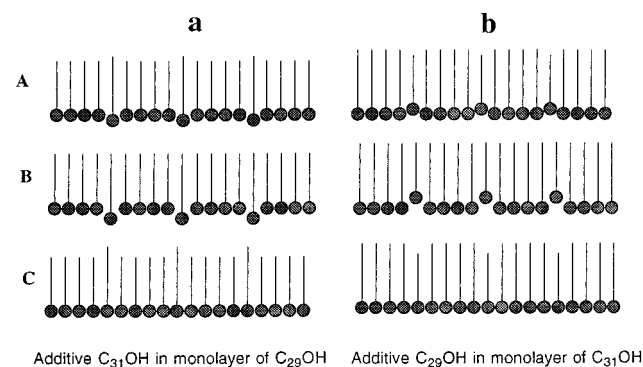


Figure 5. (a) Freezing temperatures of supercooled water drops covered by a mixture of C₂₉OH and C₃₁OH as a function of C₂₉OH percentage in the mixture. (b) Normalized number of defect-free hexagonal domains of a fixed diameter as a function of the percentage of active component in a computer-simulated random mixture of the two components.

CHART 1



the ice freezing curve in which C₃₁OH is the more effective contaminant. Here we focus only on the effect guest C₃₁OH, in the concentration range 0–10%, has on the ice nucleation temperature induced by the mixed monolayer. We have presupposed the formation of a random solid solution of the two components. The crystalline monolayers of the pure C₂₉OH and C₃₁OH amphiphiles on water are isostructural,⁹ as well as their binary mixtures in various ratios,¹⁸ according to GID measurements. These results, however, do not prove or disprove the existence of random solid solutions of the two components. On the other hand, the proposed structure is in agreement with the ice-nucleating behavior of the mixtures; had there been a strong tendency for a separation of phases, the ice-nucleating temperature would have remained in the range of the pure species. Further support in favor of a random distribution of guest molecules comes from recent surface reflectance IR measurements, complemented by GID experiments, on mixtures of C₃₁OH and C₃₂D₆₆ on water.²⁰

In order to simulate the surface composition of the mixed monolayer of host C₂₉OH and guest C₃₁OH randomly occluded

in the concentration range 0–10%, we introduced, via a random number generator, defect sites into a two-dimensional hexagonal grid of 200 by 200 lattice points.²¹ The number of defect-free hexagonal-shaped domains of fixed diameter, ranging from 9 to 45 Å, were counted for various defect concentrations and normalized to a defect-free grid, as shown in Figure 5b. The curve for a diameter of 36 Å is in best agreement with the ice-nucleating results in Figure 5a for C₃₁OH as inhibitor in the range 0–10%. Here we have assumed, on the basis of experimental data,²² that the ice-nucleating domains are by and large of a fixed size and that the ice-nucleating efficiency is proportional to the number of nucleating domains.

In conclusion, the ice-nucleating efficiency for the C₃₁OH monolayer is proportional to the number of its crystalline domains down to a concentration of 5% of C₃₁OH in an inert matrix. For the C₂₀OH monolayer, the catalytic efficiency remains constant down to a concentration of ~50% in the inert matrix, below which the ice-freezing temperature drops linearly with the number of crystallites. The results obtained from the solid solution of the C₂₉OH monolayer contaminated by C₃₁OH are consistent with an ice-nucleating monolayer domain of about ~35 Å which well matches the 25 Å domain size¹⁰ of ice parallel to its *ab* plane and the extent of the lattice fit between ice and the monolayer. These results indicate that the critical diameter of an ice nucleus, which would form under homogeneous conditions at a temperature just below 0 °C, cannot be smaller than 25–30 Å, which would correspond to a sphere containing ~450 water molecules. By comparison, clusters of water molecules formed on expansion through a nozzle incorporated a crystalline ice core of ~45 Å diameter, according to electron diffraction measurements.²³

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References and Notes

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