of new crystalline forms, this material was precipitated from aqueous solutions, by cooling, in the two experimental setups described above. X-ray powder patterns of the crystalline materials are shown in Figure 1c–e. The crystallization experiments in the open vessel yielded a new crystalline phase, which precipitated together with the known phase[10] previously defined as the γ-form[6] (Figure 1c). Such samples display four new and distinct diffraction peaks with *d* spacings of 6.0, 5.1, 5.0, and 4.2 Å.

Solid-state UV irradiation of the mixture of the crystalline phases yielded the mirror photodimer **2** (Figure 1f). This dimer must arise from the new crystalline phase because the γ-form is light stable and the diffraction peaks associated with the new phase disappear upon irradiation[11] (Figure 1d).

From the experiments performed in the closed vessels, the γ-phase precipitates, either in pure form (50% of experiments) or with only small amounts of the new phase (Figure 1e).

The formation of the mirror-symmetric β-dimer **2** from irradiation of the solutions in the open vessel and from the solid precipitated in the same vessel strongly suggests the formation of ordered two-dimensional aggregates at the air/solution interface. Furthermore, the common feature of the mirror symmetry of the dimer **2** implies that the molecules are stacked by "translation symmetry" within the clusters at the interface and in the new polymorph. Thus it is reasonable to deduce that the clusters are nuclei en route to crystal formation. Observation of these clusters by more direct methods, such as grazing incidence X-ray diffraction,[12] might provide a deeper insight into crystalline nuclei of precritical size.

Acknowledgment. We thank the U.S.–Israel Binational Science Foundation, Jerusalem, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

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Ice Nucleation: A Test To Probe the Packing of Amphiphilic Alcohols at the Oil–Water Interface

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Received July 8, 1991
Revised Manuscript Received August 20, 1991

Amphiphilic molecules tend to accumulate in the form of monolayers at the interface between water and an immiscible liquid. Such monolayers have been extensively studied by classical techniques, such as interfacial tension and surface potential measurements.[1-4] However, experimental work probing structural details on the molecular level is very limited[5,6] although some theoretical simulations of the liquid–liquid interface have been reported.[7-9]

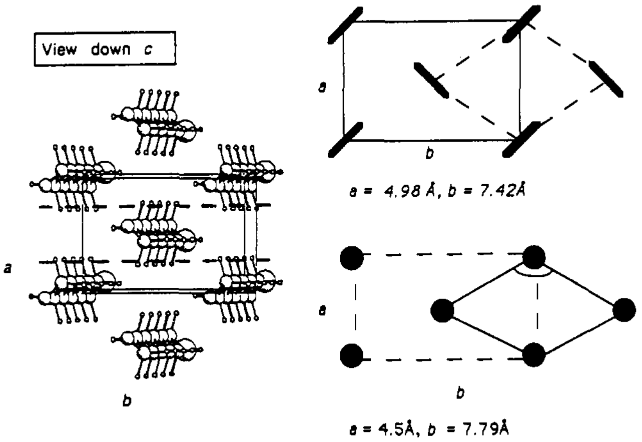

Figure 1. Packing arrangement viewed perpendicularly to the water surface of models of alcohol monolayers in crystallites formed at 5 °C over pure water (left). Schematic representation of the orthogonal packing of the hydrocarbon chains (right top). Schematic representation of the *ab* lattice of hexagonal ice (right bottom).

We have demonstrated previously that monolayers of insoluble alcohols, when deposited on water drops at the air–water interface, act as efficient ice nucleators.[10] Grazing incidence X-ray diffraction measurements have shown that at temperatures below 9 °C these alcohols self-aggregate to form two-dimensional crystalline domains whose *ab* net is close in dimension to the *ab* lattice of hexagonal ice (Figure 1). Moreover, the analysis of the grazing incidence diffraction data indicates not only a good lattice match but also a reasonable structural fit of the alcohol OH moieties to that of the ice layer.[11] Such domains may induce the formation of ice-like embryos at the interface, leading to efficient nucleation. Freezing temperatures were strikingly sensitive to minor structural changes in the amphiphilic alcohols, such as chain length, carbon parity, and surface area per molecule.

In the present study we exploit the structural match between monolayer and ice to probe the oil–water interface on a molecular level.[12] Experiments were carried out by measuring the freezing points of water drops placed in organic solutions of long-chain aliphatic alcohols. As references, the solutions of the corresponding carboxylic acids or the pure solvents have been used.

Figure 2a shows that aliphatic alcohols $C_nH_{2n+1}OH$ with $n >$ 22 nucleate ice at higher temperatures than the corresponding carboxylic acids, as was found at the air–water interface. Moreover, temperatures of freezing were observed to depend on alcohol chain length and carbon parity. The largest difference, of about 6 °C, was obtained between the freezing points induced by alcohols with $n = 30$ and $n = 31$. This experiment strongly suggests that the amphiphilic alcohols aggregate at the oil–water interface into crystalline clusters. The results also indicate that surfaces or templates created by aggregates of the odd-numbered alcohols have a better structural fit with ice than the even-numbered homologues, possibly due to somewhat different orientations of their OH groups. The fact that ice nucleation at the oil–water interface was observed with alcohols having a chain length of $n > 22$, whereas at the air–water interface it required only $n > 16$,

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(12) In contrast to our structural approach, J. Rosinski (*J. Phys. Chem.* **1980**, *84*, 1829) proposed that heterogeneous ice nucleation can take place at the liquid–liquid interface as a result of ordering by dipole moments of the organic liquid.

(13) All materials, except alcohols with $n = 23$, 29, and 31, were purchased from Sigma and were specified >98% pure. Alcohols with $n = 23$, 29, and 31 were synthesized by reducing the corresponding methyl ester with $LiAlH_4$ and purified by column chromatography on silica gel, using methylene chloride as eluent. A Mili-Q water purification system was used to get high-resistivity water.

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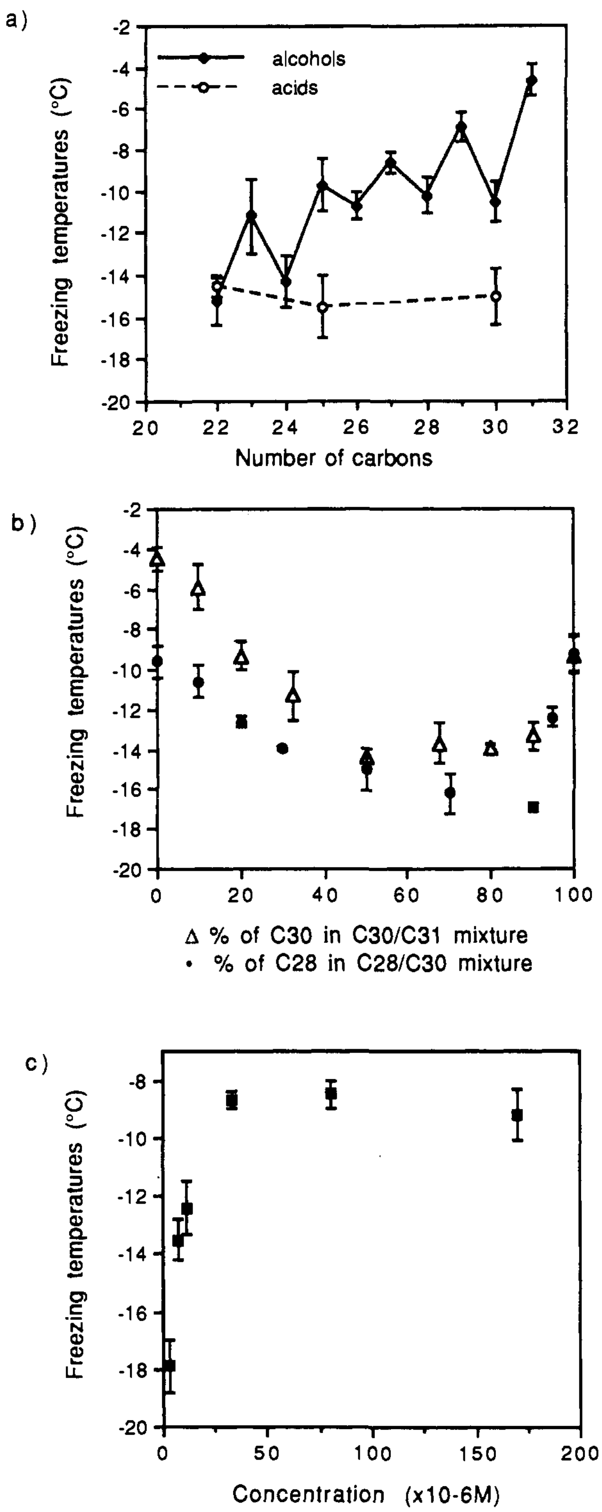

Figure 2. (a) Freezing points of supercooled 10-μL water drops in contact with 2.5 × 10^{-4} M solutions of aliphatic alcohols ($C_nH_{2n+1}OH$) and acids ($C_{n-1}H_{2n-1}CO_2H$) in 1/1 chloroform–hexane. The error bars were derived from 10–15 freezing point measurements.[13] (b) Freezing points of supercooled water drops in contact with 2.5 × 10^{-4} M solutions of mixtures in various ratios of C_{30}/C_{31} alcohols in 1/1 chloroform–hexane as depicted by the symbol Δ and mixtures of C_{28}/C_{30} alcohols in 1/1 chloroform–hexane depicted by the symbol ●. (c) Freezing points of supercooled water drops in contact with solutions of C_{30} alcohol in 1/1 chloroform–hexane as a function of concentration.

suggests that longer chains with more hydrophobic interactions are required in order to overcome the disordering effect of the organic solvents.

Table I. Freezing Points of Supercooled Water Drops in Contact with Organic Solutions of Alcohols $C_nH_{2n+1}OH$ (n = 30, 31) vs Solvents

solvent[a]	n = 30	n = 31	ref[b]
$CHCl_3$	−9.4 ± 1.0	−4.7 ± 0.6	
$CHCl_3$–hexane	−10.5 ± 1.0	−4.6 ± 0.8	−16.5 ± 2.0
$CHCl_3$–cyclohexane	−8.3 ± 0.2	−4.5 ± 0.8	
toluene	−9.1 ± 1.0	−3.7 ± 1.0	
octane	−7.2 ± 0.8	−5.7 ± 1.0	−16.6 ± 1.5
decane	−6.8 ± 0.8	−6.2 ± 1.4	−15.3 ± 2.0

[a] The solvents used were as follows: hexane, chloroform (Bio-Lab, A.R.), toluene (Frutarom, A.R.), octane, decane (Merck, C.P.). [b] As references, the freezing points of water drops placed in the pure solvents have been used.

Nucleation experiments performed under identical conditions but with organic solutions containing mixtures of alcohols with n = 30 and n = 31 in various ratios (Figure 2b) show typical "solid solution" behavior.[14] Similar behavior was obtained with solutions of mixed alcohols with chains having n = 28 and n = 30 in various ratios, although the freezing points induced by the two pure phases were the same (Figure 2b). These results suggest that aggregates of the mixed alcohols have hydroxy groups that create surfaces with a larger structural mismatch to ice than each of the pure phases.

In another series of experiments, the effect of the chemical nature of the organic solvent on ice nucleation was studied. Freezing points induced by solutions of alcohols with n = 30 and n = 31 in various solvents have been measured (Table I). When alcohols were dissolved in octane or decane, the differences in freezing points induced by alcohols with n = 30 and n = 31 almost completely disappeared. This indicates that such long-chain hydrocarbons may interact specifically with the hydrophobic tails or the end methyl groups of the amphiphiles. The hydrophobic interactions between the amphiphiles may be substituted by interactions with the long hydrocarbon solvents which diminish the original structural differences between the odd and even aggregates. The odd/even effect was observed when the alcohols were dissolved in chloroform or toluene, solvents that are chemically different from the aliphatic alcohols.

The effect of alcohol bulk concentration on the threshold freezing temperatures was also examined, as shown in Figure 2c. It is remarkable that surface accumulation of C_{30} alcohol at the octane–water interface could not be detected by interfacial tension measurements at a bulk concentration[15] of 2.5 × 10^{-4} M and at 20 °C, whereas maximum nucleation efficiencies were reached at alcohol concentrations as low as 5 × 10^{-5} M. These results suggest very low surface coverage of the alcohols and possibly small domain sizes.

We have provided evidence that long-chain amphiphilic alcohols aggregate at the oil–water interface to form structured clusters. Ice nucleation is a probe that can sense, at the molecular level, minor structural changes of such aggregates and differences in their interactions with the organic environment. Aggregation of amphiphilic molecules into ordered clusters at the oil–water interface is a phenomenon of a general nature, as demonstrated recently by "epitaxial-like" growth of glycine at the oil–water interface[16] and by topochemical photodimerization of cinnamic acids.[17] Grazing incidence diffraction measurements are currently being undertaken to detect, directly, such ordered clusters. This approach opens also possibilities to study other types of oil–water interfaces, such as emulsions.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the U.S.–Israel Binational Science Foundation, Jerusalem, for financial support and Edna Shavit for the synthesis of alcohols.

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