Absolute Orientation of Molecules of Amphiphilic Alcohols in Crystalline Monolayers at the Air–Water Interface

Ron Edgar,[#] Jung Y. Huang,[†] Ronit Popovitz-Biro,[#] Kristian Kjaer,[‡] Wim G. Bouwman,[‡] Paul B. Howes,[‡] Jens Als-Nielsen,[§] Y. Ron Shen,^{*,†} Meir Lahav,^{*,#} and Leslie Leiserowitz^{*,#}

Department of Materials and Interfaces, The Weizmann Institute of Science, 76100 Rehovot, Israel, Department of Physics, University of California, Berkeley, California 94720, Condensed Matter Physics and Chemistry Department, RisØ National Laboratory, DK 4000 Roskilde, Denmark, and H. C. Ørsted Laboratory, Niels Bohr Institute, DK 2100 Copenhagen, Denmark

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The absolute orientations of the amphiphilic molecules α -hydroxy ω -bromo alcohols BrC_nH_{2n} OH, n = 21, 22, and the alkyl hydroxy esters C_mH_{2m+1}COO(CH₂)_nOH, m = 14, 15, n = 10, in crystalline monolayer forms on water have been determined, the former by grazing incidence X-ray diffraction (GIXD) and the latter by sum frequency generation (SFG). The assignment was made for the alkyl hydroxy esters by establishing the polar angle between the terminal CH₃-C bond and the normal to the plane of the monolayer; for the bromo alcohols the assignment was made by a determination of the two-dimensional crystal structure via X-ray structure factor calculations. The SFG results are in agreement with reported GIXD and lattice energy analyses of the alkyl hydroxy esters m = 19, n = 9, 10. These studies have further revealed the absolute orientation of the alcohol C-OH bonds at the water surface, which in turn can be correlated with the ice-nucleating behavior of the monolayers on supercooled water drops in terms of the odd and even values of n.

Introduction

In general, the overall packing arrangements of long-chain amphiphilic molecules $C_nH_{2n+1}X$ at the air—solution interface can, given the molecular conformation, be established by grazing incidence X-ray diffraction (GIXD) using synchrotron radiation. However, the amount of diffraction data measured is generally insufficient to differentiate between the correct azimuthal orientation of the molecular chain and the alternative obtained by rotation of 180° about the long-chain axis. This uncertainty can lead to an ambiguity in determination of the orientation of the polar headgroup X in contact with the liquid surface. Here we present a study employing various approaches for the assignment of the absolute azimuthal orientation of long-chain alcohols on water.

Crystalline monolayers of alcohols $C_nH_{2n+1}OH$ (n = 13-31) are very efficient ice nucleators of supercooled water drops^{1,2} by virtue of a lattice match between the unit cell of the crystalline monolayer cell and the *ab* lattice of hexagonal ice.³ On cooling, the temperature at which the water drops froze was found to be dependent on chain length and whether *n* is odd or even (Figure 1). GIXD measurements of the alcohol monolayers on water at temperature of 5 °C revealed 2-dimensional crystalline self-assembly.^{3,4} The GIXD patterns of the monolayers of the two alcohols n = 30, 31, were essentially identical, indicating very similar monolayer packing arrangements. This trend is prevalent for chains differing in length by only one methylene (CH₂) group throughout the series, contrary to the large difference in their corresponding ice-nucleating properties. These observations could only be explained by assuming that



Figure 1. Freezing temperatures of supercooled water drops covered by monolayers of amphiphilic alcohols $C_n H_{2n+1}OH$, n = 13-31, and the ω -bromo alcohols Br(CH₂)₂₁OH and Br(CH₂)₂₂OH. The temperature referred to is that at which, on slow cooling at 2 °C/min, the water drops were observed to solidify.^{1,2}

the *hydrocarbon chains*, C_nH_{2n+1} , of both the odd and even series adopt similar azimuthal orientations, which would lead to a systematic difference in the orientations of their CH₂OH polar groups in contact with the water subphase.

Further evidence for the role played by the orientation of the C–OH group is provided by the ice-nucleating properties of monolayers of the alkyl hydroxyl esters² $C_mH_{2m+1}COO(CH_2)_n$ -OH (hereafter abbreviated C_mCOOC_nOH). The onset temperature of ice formation using these monolayer systems depends on the odd and even values of *n* but not on that of *m* (Table 1).² The molecules of the two ester alcohols m = 19, n = 9, 10 on water each form crystalline monolayers and pack in similar herringbone arrangements (Figure 2, top right) in plane group $p1 \ 1g$ (namely, a primitive cell *p*, with a glide *g* perpendicular to the *b* axis), as determined by GIXD. The chains are tilted by angle $T \cong 29^{\circ}$ from the layer normal; their absolute orientations

[#] The Weizmann Institute of Science.

[†] University of California, Berkeley.

[‡] RisØ National Laboratory.

[§] Niels Bohr Institute.

TABLE 1: Freezing Temperatures (FT) of Supercooled Water Drops Covered by Monolayers of Various Alkyl Ester Alcohols (C_mCOOC_nOH) and α -Hydroxyl ω -Bromo Alcohols (BrC_nOH)

entry ^a	compound	FT^{b} (°C)
1	C ₁₁ COOC ₁₀ OH	-4.2 ± 0.6
2	C ₁₄ COOC ₁₀ OH	-4.0 ± 0.7
3	C ₁₉ COOC ₁₀ OH	-4.0 ± 0.7
4	C ₁₉ COOC ₁₂ OH	-4.3 ± 0.9
5	BrC ₁₀ COOC ₁₀ OH	-4.6 ± 0.9
6	C ₁₄ COOC ₉ OH	-10.0 ± 0.8
7	C ₁₉ COOC ₉ OH	-9.0 ± 0.8
8	C ₁₉ COOC ₁₃ OH	-8.0 ± 0.4
9	C ₂₁ COOC ₉ OH	-8.8 ± 0.8
10	BrC ₂₁ OH	-6.4 ± 0.9
11	BrC ₂₂ OH	-4.9 ± 1.0

^{*a*} Entries 1-9 are divided into two groups, *n* even and *n* odd. ^{*b*} The water drops were cooled at a rate of 2 °C/min until they were observed to solidify as described in refs 1 and 2.



Figure 2. (Top, left and center) Two-dimensional crystal structures on water of the alkyl ester alcohols (abbreviated) $C_{19}COOC_nOH$, n =9, 10, viewed along the *b* axis. The molecules related to each other by glide symmetry along the *a* axis are in full and dashed lines. (Top, right) View down the molecular axis depicting the herringbone arrangement induced by the glide plane along *a*. Of the two monolayers, $C_{19}COOC_nOH$, n = 9, 10, the latter is the better ice nucleator (see Table 1). (Bottom) Angle *t* which the terminal $C-CH_3$ bond makes with the normal to the layer plane for molecules C_mCOOC_nOH , m =odd, even. The molecular chain axis is tilted by angle *T* from the normal to the layer plane, in the direction of the *a* axis. The molecular plane is not parallel to the plane defined by the chain axis and the molecular layer normal, as is also evident from the view of the herringbone arrangement shown in top, right.

were obtained³ from differences in lattice energy, albeit as low as 1-2 kcal/mol, of the two possible azimuthal orientations of each molecule. These differences arise primarily from interactions involving the COO groups, yielding the packing arrangements with the more favorable chain orientation shown in Figure 2 (top left, center) and therefore distinctly different CH₂OH orientations for n = 9, 10. The remaining moiety C₁₉COOC₉ common to both structures is arranged in the same way. It is noteworthy that the derived chain orientation is the same as in the intralayer molecular arrangements of the three-dimensional crystal structures of analogous compounds, C_mH_{2m+1}COOCH₂-CH₃ (m = 17, 21).^{5,6}

The polar angle between the C-CH₃ bond and the normal to the monolayer plane of the ester alcohols C_mCOOC_nOH , m = 19, n = 9, 10, defined as t is decidedly different for the derived chain orientation and its azimuthal alternative. By similar reasoning, given that the absolute azimuthal orientation of the chain does not depend on the odd or even value of m according to the ice nucleation behavior (vide supra), the angle t should be distinctly different for m odd and m even as shown in Figure 2, bottom. To confirm this hypothesis and thus establish the absolute orientation of the ester alcohol C_mCOOC_n -OH molecules in a monolayer form on the water surface, the absolute chain orientation of the hydroxyl alkyl ester molecules C_mCOOC_nOH , m = 14, 15, n = 10, were experimentally ascertained by sum frequency generation (SFG) measurements, as described herein.

The ambiguity in orientation of the alcohol molecular chain appreciably tilted from the normal to the layer plane may also be resolved by GIXD, through the introduction of a heavy atom X-ray scatterer at the end position of the chain. The chains of the pure alcohols $C_nH_{2n+1}OH$, n = 19, 20, tilt at an angle *T* of about 20° from the layer normal.⁴ On the assumption that the bromo derivatives $BrC_nH_{2n}OH$ (abbreviated BrC_nOH) adopt arrangements similar to that of the pure alcohols, model X-ray structure factor calculations suggested that the two azimuthal orientations of the two compounds, BrC_nOH , n = 21, 22, have distinctly different Bragg rod profiles, as shall be shown. The ice-nucleating temperatures of monolayers of these two bromo alcohols were found to be -6.4 and -4.9 °C, respectively (Table 1, Figure 1).

Experimental Methods

Grazing Incidence X-ray Diffraction (GIXD). The experiments were performed on the liquid surface diffractometer at the undulator beamline BW1, Hamburg Synchrotron Radiation Laboratory (Hasylab), DESY. A sealed and thermostated Langmuir trough equipped with a Wilhelmy balance was mounted on the diffractometer. The amphiphilic films on the water surface were measured with an average area per molecule of 25 Å² and no observable surface pressure. Essential information on the GIXD method is presented in the Appendix. A detailed description of the GIXD method is given elsewhere.^{7,8}

Infrared–Visible Sum-Frequency Generation (IV-SFG) Data Collection. The IV-SFG measurements were carried out on an apparatus that incorporated a laser system that produces visible ($0.532 \,\mu$ m) and infrared picosecond pulses at 20 pulses/ s. The infrared beam is tunable from 2.5 to 8 μ m with a 5-cm⁻¹ line width⁹ and can deliver about 70 μ J/pulse to a sample. The visible and infrared pulses were overlapped spatially and temporally on the sample surface with beam diameters of about 600 and 200 μ m, respectively, and four incident angles $\Theta_{vis} =$ 42° and $\Theta_{ir} = 51°$. The SF output was collected and recorded by a gated detection system. A combination of spatial and spectral filtering was employed to discriminate against noise from laser scattering or fluorescence. A description of the second-order nonlinear optical process of IV-SFG is given in the Appendix.



Figure 3. Sum-frequency spectra (*ssp*, filled squares; *ppp*, filled triangles) of monolayers of alkyl ester alcohol amphiphiles on water deposited for a nominal surface area of 31 Å²/molecule: (a) $C_{14}COOC_{10}$ -OH monolayer, the positions of frequencies 2850, 2881, 2925, 2942, and 2963 cm⁻¹ are marked; (b) $C_{15}COOC_{10}OH$ monolayer.

Results

IV-SFG Vibrational Spectra of Alkyl Hydroxyl Ester C_mCOOC_nOH Monolayers. The monolayers on water of the two alcohols C₁₄COOC₁₀OH and C₁₅COOC₁₀OH have been studied by IV-SFG. They were spread on water at 2 °C in a Langmuir trough. The *ssp* and *ppp* spectra for $C_{14}COOC_{10}OH$ with a surface coverage of 31 $Å^2$ /molecule, which is 70% of a fully compact monolayer (22 Å²/molecule), are presented in Figure 3a. The spectra for a full monolayer (not shown) are the same except that the signal intensity increases by a factor of 2. Several spectral features are clearly observed, all of which can be assigned to the CH stretches.¹⁰ Those at 2925 and 2963 cm⁻¹ arise from the anti symmetric stretch of CH₂ and CH₃, while the features at 2881 and 2942 cm⁻¹ arise from the symmetric stretch of CH₃ (s-CH₃) and the Fermi resonance between the s-CH₃ stretch and the overtone of the CH₃ bending mode, respectively. There is also a weak shoulder at 2850 cm⁻¹ that can be assigned to the symmetric CH₂ stretch. In view of the very weak CH₂ modes in the spectrum, we can conclude that the alkyl chains of $C_{14}COOC_{10}OH$ must be in a nearly all-trans configuration. By fitting the measured spectra using eq 1 (see Appendix), we can determine the magnitude of $|\chi_{ppp}^{(2)}/\chi_{ssp}^{(2)}|$ for the *s*-CH₃ mode to be 0.43 and accordingly the polar angle of the terminal CH₃ group of C₁₄COOC₁₀OH to be $t = 9^{\circ}$. In a more rigorous analysis, the crystalline structure of the monolayer as revealed by the GIXD study³ and the possible domain structure of the monolayer were included, but we found no significant change from that with a macroscopically 'isotropic' film (akin to a 'two-dimensional powder' as described in the Appendix on GIXD) in which the chain axis adopts all possible orientations about the surface normal for a fixed tilt angle T. We also established that $\chi_{ssp}^{(2)}$ and $\chi_{ppp}^{(2)}$ have opposite signs from the SFG results of the C₁₄COOC₁₀OH monolayer using an infrared input with p-polarization and a visible input with a mixed polarization.

For a C₁₅COOC₁₀OH monolayer with 31 Å²/molecule (70% of a nominal full monolayer coverage), the *ssp* SFG spectrum (Figure 3b) is about 1 order of magnitude weaker than that from C₁₄COOC₁₀OH (Figure 3a). This is presumably because the H₃C-C bond in this case lies close to the surface plane. Indeed, if the all-trans alkyl chains have the same orientation in C₁₅-



Figure 4. Calculated χ_{ppp}/χ_{ssp} of the *ppp* and *ssp* susceptibilities at *s*-CH₃ stretch as a function of the polar angle of methyl group with varying $R = \alpha_{\eta\eta\sigma}^{(2)}/\alpha_{sss}^{(2)}$ and effective index of refraction of monolayer. The filled squares denote the measured values for the C₁₄COO₁₀OH monolayer. The polar angle of the methyl group of this monolayer was deduced from the analysis of the SFG data.

COOC₁₀OH as in C₁₄COOC₁₀OH that was measured by SFG and GIXD (vide infra), the CH₃ terminal group of C₁₅COO₁₀-OH should have a polar angle *t* in the range of 60°. With this orientation, we indeed find from our estimate an SHG spectrum for C₁₅COOC₁₀OH 1 order of magnitude smaller than that for C₁₄COOC₁₀OH.

The influences of local field corrections on our SFG data analysis had been evaluated, and the local field corrections were found to be negligible. Figure 4 describes the calculated ratio $\chi_{ppp}^{(2)}/\chi_{ssp}^{(2)}$ of the *ppp* and *ssp* susceptibilities at the *s*-CH₃ stretch as a function of the polar angle of the methyl group. The local field effect was taken into account by using an effective index of refraction *n'* for the monolayer. The filled squares denote the measured $\chi_{ppp}^{(2)}/\chi_{ssp}^{(2)}$ for the C₁₄COOC₁₀OH monolayer on water subphase (at temperatures of 2 and 22 °C). The data agree fairly well with the calculated curve (solid line) with an effective index of refraction taken to be 1. We consider this conclusion to be reasonable in view that most of the chemical bonds in the molecule are saturated and thus have small bond polarizabilities and the methyl group lies high above the alkyl chain in the all-trans configuration. Note that a 70% surface coverage in our monolayers may also reduce the influence of local field effect.

Within our experimental accuracy, we also found our analysis results do not change significantly with $R = \alpha_{\eta\eta5}^{(2)}/\alpha_{SSS}^{(2)}$. This can be better appreciated in Figure 4, where the calculated curves of $\chi_{ppp}^{(2)}/\chi_{ssp}^{(2)}$ with *R* varying from 2.0 to 3.0 are presented.

We have also detected the 1735-cm⁻¹ stretch mode of C=O on the chains of C₁₄COOC₁₀OH and C₁₅COOC₁₀OH, as presented in Figure 5a,b. The ratio between the ssp (filled triangles) and ppp (filled circles) signals is close to a value of 1 for both monolayers and suggests that the C=O bonds in both monolayers tilt from the film normal with a large angle (> 60°). If the two C=O bonds point to the same direction, then in mixed monolayers of C14COOC10OH and C15COOC10OH at 70% compactness the SFG spectrum should therefore be fairly constant with respect to the molar fraction of C14COOC10OH component, assuming that the chain orientation remains unchanged. This was indeed observed, as shown in Figure 5c for a variety of mixtures. The observed variation of the spectrum with composition is partly the result of poor control of the overall surface density in our experiment. It is also an indication that the C=O orientation is more disordered, and accordingly



Figure 5. *ssp* (filled triangles) and *ppp* (filled squares) sum-frequency spectral profiles in the C=O stretch region from a monolayer of (a) $C_{14}COOC_{10}OH$ and (b) $C_{15}COOC_{10}OH$ at a nominal surface area of 31 Å²/molecule. The solid and dashed lines in parts a and b are the nonlinear least-squares fits of the profiles to eq 3 given in the Appendix. (c) Measured *ssp* spectral profiles from binary mixtures of $C_{14}COOC_{10}OH$ are plotted as a function of the molar fraction of $C_{14}COOC_{10}OH$.

the chains less well aligned, in the mixed monolayers than in the pure $C_{14}COOC_{10}OH$ or $C_{15}COOC_{10}OH$ monolayer. Nevertheless, the presence of a relatively strong signal from the 1:1 mixture shows that the C=O carbonyl bonds of the $C_{14}COOC_{10}$ -OH and $C_{15}COOC_{10}OH$ molecules are essentially parallel to each other and is further evidence that the overall chains of the two molecules have the same azimuthal orientation. Had their azimuthal orientations differed by 180°, the SFG signal from the C=O bond would have been essentially zero.

GIXD Measurements on the Alkyl Ester Alcohols C_m **-COOC**_n**OH.** To ascertain that the alkyl ester alcohols C_m -COOC_nOH, m = 14, 15, n = 10, studied by SFG form monolayer crystal structures on water akin to that of the longer chain molecules m = 19, n = 9, 10, GIXD measurements were performed on the uncompressed films of the two amphiphiles m = 11, 14, n = 10. Their GIXD patterns (not shown) verify the formation of crystalline monolayers with packing arrangements very similar to those of the longer chain analogues according to cell dimensions, chain tilt, and plane group (compare entries 1, 2 and 4, 5 in Table 3).

The results obtained by analysis of the SFG data on the ester alcohols C_mCOOC_nOH , m = 14, 15, n = 10, are in agreement with the assignment of absolute azimuthal orientation of C₁₉-COOC_nOH, n = 9, 10, by lattice energy calculations performed on the monolayer structures determined via the GIXD data and with the deduction that the absolute azimuthal angle is fixed by the molecular interactions involving the ester COO groups.³ The angle *t* between the normal to the layer plane and the C-CH₃ bond for the molecules m = 15, 19 is about 60° and the angle *t* for m = 14 is 9° according to SFG, which is sufficiently close to 21° as would have been deduced from the two-dimensional crystal structure of $C_mCOOC_{10}OH$ but with m = 14, rather than m = 19 (compare the *t* values of entries 1–4 in Table 3 and see Figure 2, top).

TABLE 2: Molecular Chain Orientation^{*a*} Listing Observed and Alternative Values of Polar Angle *t* and Chain Tilt *T* in Three-Dimensional Crystal Structures Containing an ω -Bromo Substituent

compound	t (deg)	$t_{\rm alt}({\rm deg})$	T (deg)	refcode ^b
Br(CH ₂) ₁₈ Br	75	37	50	PODMAW
Br(CH ₂) ₁₀ COOH	74	42	50	BUNDAC
Br(CH ₂) ₁₁ OH	73	40	49	BUNDEC10
[Br(CH ₂) ₁₀ COOCH ₂ CH] ₂ OH	66	42	43	BUDGLY
Br(CH ₂) ₁₀ COOCH ₂ CHOHCH ₂ OH	60	56	27	BRUDAG

^{*a*} *t* is the observed polar angle between the CH₂–Br bond and the layer normal and t_{alt} is the alternative value thereof for the molecule rotated by 180° about its chain axis. *T* is the tilt angle between the chain axis and the layer normal. ^{*b*} Refcode in the Cambridge Structural Database (CSD).

 TABLE 3: General Packing Characteristics^a of the Alkyl Ester Alcohols (1–7) and the Bromo Alcohols (8, 9)

entry	compound	a (Å)	b (Å)	plane group	T (deg) via GIXD	t (deg)	$t_{\rm alt} ({ m deg})$
1	C19COOC9OH	5.79	7.50	p11g	30	58	22
2	C ₁₉ CO ₂ C ₁₀ OH	5.69	7.49	p11g	28	58	21
3	C15CO2C10OH					60^{b}	
4	C14CO2C10OH	5.75	7.46	p11g	28	9	
5	C11CO2C10OH	5.85	7.48	p11g	29		
6	BrC10CO2C10OH	5.61	7.33	p11g	28		
7	BrC11CO2C10OH	6.60	7.49	p11g	41		
8	BrC ₂₁ OH	5.94	7.46	p11g	34	68	25
9	$BrC_{22}OH~(\alpha\text{-phase})$	5.84	7.44	p11g	33	65	26

^{*a*} Including cell dimensions, plane group, chain tilt angle *T*, and polar angle *t* between the CH₂–Br, or CH₂–CH₃, bond and the normal to the layer plane. t_{alt} is the alternative value of *t* for the molecule rotated by 180° about its chain axis. The chain tilt angle *T* was determined by GIXD for entries 1, 2, and 4–9. The bond polar angle *t* was determined by GIXD combined with lattice energy calculations for entries 1 and 2, by SFG for entries 3 and 4, and by GIXD for entries 8 and 9. ^{*b*} The polar angle *t* of 60° was not determined directly from the SFG measurements as described in the text.

Structure Determination of the Bromo Alcohol Monolayers. The amphiphiles BrC_nOH , n = 21, 22, were each spread on the water surface from dilute chloroform solutions (10^{-4} M) at room temperature. The GIXD measurements were performed after cooling the subphase to 5 °C and with no detectable surface pressure. The bromine derivatives were found to be extremely sensitive to the incident X-ray beam, the films suffering damage throughout the measurement. The Bragg peak intensities of different reflections were scaled according to the duration of the exposure to the X-ray beam.¹¹ This beam damage does not adversely affect the outcome of our analysis, which depends primarily on the shapes of the individual Bragg rod intensity profiles.

The positions of the four observed Bragg peaks of the film formed by BrC₂₁OH were indexed to yield a rectangular cell with dimensions listed in Table 3. The film is a monolayer ~ 25 Å thick according to the fwhm = 0.24 Å⁻¹ along q_z of the Bragg rods of strong low-order $\{1,1\}$ and $\{0,2\}$ reflections (see Figure 6b). The positions of the intensity maxima of these Bragg rod profiles indicate that the chains are appreciably tilted from the layer normal by an angle T of 34° in the a direction, in agreement with the dimension of the a axis.¹² The unit cell dimensions and the direction and magnitude of the chain tilt angle of BrC₂₁OH are very similar to that of the two-dimensional crystal structure of $C_{19}COOC_nOH$, n = 9, 10 (see entries 1, 2, 7 in Table 3), and consequently "fingerprint" evidence of a similar herringbone packing arrangement in plane group *p*11*g*. The molecular models for the two possible azimuthal orientations about the chain axis, differing by a rotation of 180°, are



Figure 6. Br(CH₂)₂₁OH: (a) molecular models for the two possible azimuthal orientations (left, right) viewed along the *b* axis, the nearest-neighbor molecules along the *a* direction are related by glide symmetry; (b) corresponding calculated (solid line) Bragg rod intensity profiles and the measured values (crosses).

shown in Figure 6a. Each model was used to compute, by X-ray atomic structure factor calculations, the Bragg rod intensity profiles of the three strong reflections {1,1}, {0,2}, and {1,2}, shown in Figure 6b superimposed on the measured profiles.¹³ The two azimuthal orientations yield the same calculated Bragg rods of the {0,2} reflection, which also match the observed profile; the calculated {1,1} and {1,2} Bragg rods of the model orientation shown in Figure 6a, left, fit better to the observed data than the alternative model (Figure 6a, right). Note that the discrepancy between the observed and calculated Bragg rod



Figure 7. Br(CH₂)₂₂OH: two-dimensional intensity distribution $I(q_{xy}, q_z)$ of the GIXD pattern. The two low-order reflections are shown for the monolayer (α) and multilayer (β) phases.

profiles appears more significant for $\{1,1\}$ than for $\{1,2\}$. The azimuthal orientation of BrC₂₁OH is hence directly determined from the GIXD data.

The amphiphile BrC₂₂OH crystallizes in two coexisting phases when spread on the water surface at submonolayer surface coverage, according to the GIXD pattern (Figure 7). The fwhm of the two Bragg rods at $q_{xy} = 1.36$ and 1.69 Å⁻¹ correspond to a monolayer α -phase ~25 Å thick, whereas the Bragg rods at $q_{xy} = 1.41$ and 1.71 Å⁻¹ arise from a β -phase two to three layers thick according to their fwhm. The α -phase is isostructural to the monolayer of $BrC_{21}OH$; it gave rise to four diffraction peaks indexed $\{1,1\}$, $\{0,2\}$, $\{1,2\}$, and $\{1,3\}$, corresponding to a rectangular unit cell of dimensions listed in Table 3. The molecular chains are tilted from the normal to the surface plane by an angle T of 33° in the a direction according to the positions of the q_z maxima of the Bragg rods. Once again, we established the molecular azimuthal orientation of BrC₂₂-OH by X-ray atomic structure factor calculations. The fit to the observed data (Figure 8b, left) is superior for the orientation shown in Figure 8a, left, which proved to be the same as that of $BrC_{21}OH$ for their common moiety $BrC_{21}H_{42}$.

The structure of the multilayer β -phase of BrC₂₂OH could not be unambiguously determined from the eight observed Bragg reflections; nevertheless, unit cell dimensions a = 5.56 Å, b =7.36 Å and a molecular tilt *T* of ca. 30° from the surface normal, in the *a* direction, could be extracted.

According to the GIXD analysis of the monolayers of BrC₂₁-OH and BrC₂₂OH on water, the molecular chains are oriented such that the C–Br bonds make a steep angle *t* of 66° with the normal to the monolayer plane (see Figures 6a, 8a and entries 7, 8 in Table 3), pointing toward the uppermost CH₂ group of a neighboring glide-related molecule, where the Br···CH₂ distance is ca. 3.9 Å (Figure 9, left). The alternative azimuthal orientation (Figure 9, right) would increase this distance to about 5 Å. The steep *t* angle of the C–Br terminal bond vis-à-vis the layer normal is also prevalent in all three-dimensional crystal structures containing an ω -bromo hydrocarbon chain, found in the Cambridge structural database (CSD),¹⁴ listed in Table 2.

Discussion

We have found that in the monolayers of the alkyl ester alcohols $C_m COOC_n OH$ the terminal C-CH₃ bond makes a small angle *t* of 10-20° with the normal to the layer plane for *m* even and a large angle of about 60° for *m* odd (see Table 3 and Figure 2).

The moieties BrC_nH_{2n} , n = 21, 22, of the bromo alcohol monolayers are both oriented in the same way, with the C–Br



Figure 8. Br(CH₂)₂₂OH (α -phase): (a) molecular models for the two possible azimuthal orientations (left, right) viewed along the *b* axis, the nearest-neighbor molecules along the *a* direction are related by glide symmetry; (b) corresponding calculated (solid line) Bragg rod intensity profiles and the measured values (crosses).

bond making a steep angle of about 65° with the normal to the layer plane (see Table 3). The requirement for the C–Br bond to be steeply tilted vis-à-vis the layer normal leading to the packing shown in Figure 9, left, is more pronounced than for



Figure 9. Br(CH₂)₂₂OH: the intermolecular distances (in Å) of the monolayer structure as determined by the GIXD results are shown on the left; the alternative arrangement, in which the molecule is rotated by 180° about its chain axis, is on the right. (Top) View along the *b* axis, in which only the top part of the chain is shown. (Bottom) View along the molecular chain axis showing the herringbone arrangement. The open circles denote the bromine atoms.

the C-CH₃ bond according to the GIXD data of the monolayers of BrC₁₀COOC₁₀OH and BrC₁₁COOC₁₀OH.¹⁵ The finding that the moieties BrC_nH_{2n} , n = 21, 22, are both oriented in the same way means that their terminal hydroxyl groups C-OH at the water surface are differently oriented (Figures 6a, 8a, left). We may correlate these results with their ice-nucleating behavior and with the structural and ice-inducing properties of the alkyl ester alcohols. First we note the similar monolayer packing arrangements of the bromo alcohols BrC_nOH , n = 21, 22, and the alkyl ester alcohols $C_m COOC_n OH$, m = 19, n = 9, 10 and m = 11, 14, n = 10 (see Figures 2, 6a, 8a and Table 3). These structures exhibit two distinctly different C-OH orientations: one where the C-OH bond makes a shallow angle with the plane of the water surface (Figure 2, n = 10, Figure 8a, left) and the other where the C-OH bond points vertically into the water subphase (Figure 2, n = 9, Figure 6a, left). The monolayers of the former are the more efficient ice nucleators according to Table 1 (compare entries 3, 11 vs 7, 10, respectively).

In conclusion we have shown that it is possible to establish the absolute azimuthal orientation of chainlike amphiphilic molecules by a variety of different yet complementary techniques. We plan to extend the SFG studies to the monolayers of the alcohols $C_nH_{2n+1}OH$ and their methoxy derivatives $C_nH_{2n+1}OCH_3$.

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Appendix

The glancing angle α_i of the monochromated X-ray beam ($\lambda = 1.34$ Å) was adjusted to be approximately equal to $0.85\alpha_c$ (where α_c is the critical angle for total reflection) which maximizes the surface sensitivity. The dimensions of the footprint of the incoming X-ray beam on the liquid surface were $\sim 5 \times 50$ mm². GIXD diffraction peaks were obtained from two-dimensional (2D) crystallites, which have a random orienta-

tion about the water surface normal and thus are described as a 2D 'powder'. The scattered intensity was detected by a position-sensitive detector (PSD) along the vertical component of the X-ray scattering vector, $q_z \approx (2\pi/\lambda) \sin \alpha_f$, where α_f is the angle between the horizontal plane and the diffracted beam. Measurements were performed by scanning over a range along the horizontal scattering vector, $q_{xy} \approx (4\pi/\lambda) \sin \theta_{xy}$, where $2\theta_{xy}$ is the angle between the incident and diffracted beams projected onto the horizontal plane. Note that the scattering vector q = $q_{xy} + q_z$. The diffraction data are represented in two ways: the GIXD pattern I(qxy) obtained by integrating over the whole q_z window of the PSD shows Bragg peaks; Bragg rod intensity profiles are the scattered intensity I(qz) recorded in channels along the PSD but integrated across the q_{xy} range of each Bragg peak. The GIXD pattern can be also presented as a twodimensional intensity distribution $I(q_{xy}q_z)$.

Several different types of information may be extracted from the measured profiles.^{5,6} The $2\theta_{xy}$ (or q_{xy}) positions of the Bragg peaks yield the lattice repeat distances $d = 2\pi/q_{xy}$ which can be indexed by two Miller indices h,k to yield the unit cell. The fwhm of the Bragg peaks along $q_{xy'}fwhm(q_{xy})$ yields an estimate of the 2D crystalline coherence length, $L_{xy} \approx 0.88 \cdot 2\pi/fwhm(q_{xy})$. The *fwhm* of the Bragg rod intensity profile along q_z gives an estimate of the crystallite thickness $L_z \approx 0.88 \cdot 2\pi/fwhm(q_z)$.

The intensity at a particular value of q_z in a Bragg rod, corrected for variations in Lorentz factor, scattering area, and polarization, determines the square of the molecular structure factor^{7,8} $|F_{hk}(q_z)|$. The intensity profiles $I_{hk}(q_z)$ along the Bragg rod as a function of q_z (i.e. the Bragg rod profile) may thus provide precise information on the molecular chain packing by applying rigid body refinement for an atomic molecular model.

Infrared–Visible Sum-Frequency Vibrational Spectroscopy. IV-SFG is a second-order nonlinear optical process in which an infrared beam at frequency ω_{ir} and a visible beam at frequency ω_{vis} overlap in a medium and generate an output at the sum-frequency $\omega_s = \omega_{vis} + \omega_{ir}$.¹⁶ By symmetry, it is forbidden in media with an inversion center but is necessarily allowed at a surface or interface and therefore can be used to probe surfaces and interfaces. For SFG in the reflected direction, the signal is proportional to the absolute square of the effective surface susceptibility, $\chi_s^{(2)}$. Pronounced resonance in $\chi_s^{(2)}$ can be observed if ω_{ir} scans over a surface vibrational mode. In general, the SFG signal can be described by¹⁶

$$S \propto |\chi_s^{(2)}|^2 = |\chi_{nr} + \sum_q \frac{A_q}{(\omega_{\rm ir} - \omega_q + i\Gamma_q)}|^2 \qquad (1)$$

where χ_{nr} is the nonresonant background and A_q , ω_q , and Γ_q denote the resonant amplitude, frequency, and damping constant of the *q*th resonant mode. These parameters can be determined from a fit of the measured spectrum to eq 1.

The nonlinear susceptibility $\chi_s^{(2)}$ is related to the molecular nonlinear polarizability $\alpha^{(2)}$ by the expression

$$\chi_{s,ijk}^{(2)} = NL_i(\omega_s)L_j(\omega_{vis})L_k(\omega_{ir})\sum_{\xi,\eta,\varsigma} \langle i\cdot\xi\rangle\langle j\cdot\eta\rangle\langle k\cdot\varsigma\rangle\alpha_{\xi\eta\varsigma}^{(2)}$$
(2)

where *N* is the surface density of molecules, $l_{ij}k$ and ξ,η,ζ refer to the laboratory and molecular coordinates respectively, $L_i(\Omega)$ denotes the transmission Fresnel factor at the interface for the wave at frequency Ω and polarized along *i*, and the angular brackets refer to an orientational average of the molecules. In cases where only few $\alpha_{\xi\eta\varsigma}^{(2)}$ elements are nonvanishing by





symmetry, eq 2 permits the determination of average molecular orientation from the measured $\chi^{(2)}_{s,iik}$.

In the current study, we are interested in the orientation of the alcohol terminal CH₃ group whose coordinates and angles relative to the *xy* plane of the water surface are given in Scheme 1. For the symmetric stretch mode of CH₃ (*s*-CH₃), the nonvanishing elements of the nonlinear polarizability are $\alpha_{555}^{(2)}$ and $\alpha_{\xi\xi\xi\varsigma}^{(2)} = \alpha_{\eta\eta\varsigma}^{(2)}$ with ζ along the symmetric axis of CH₃. They are related to the nonlinear polarizability elements $\alpha_{\rho\rho\rho}^{(2)}$ and $\alpha_{\mu\mu\rho}^{(2)} = r\alpha_{\rho\rho\rho}^{(2)}$ of each CH bond with ρ along the bond direction, by the expressions¹⁷

$$\alpha_{\rm SSS}^{(2)} = 3C_{\rm SSS}$$

 $\alpha^{(2)}_{\rho\rho\rho}$

$$\alpha_{\eta\eta\varsigma}^{(2)} = \alpha_{\xi\xi\varsigma}^{(2)} = 3C_{\eta\eta\varsigma}$$

 $\alpha^{(2)}_{\rho\rho\rho}$ with

$$C_{\text{sss}} = \cos^3 \Lambda + r \sin^2 \Lambda \cos \Lambda$$
$$C_{\eta\eta\varsigma} = [\sin^2 \Lambda \cos \Lambda + r(\cos \Lambda + \cos^3 \Lambda)]/2 \qquad (3)$$

where $\Lambda = 71^{\circ}$ is the angle between ρ , the bond direction, and ζ is the symmetry axis of the methyl group (Scheme 1). The quantity *r* can be obtained from the ratio of the transverse and longitudinal Raman polarizability components associated with the CH bond stretch, $r = (f\alpha^{(1)}/fQ)_{\mu\mu\prime}/(f\alpha^{(1)}/fQ)_{\rho\rho} = 0.116$. From the value we then find¹⁸ from eq 3 $R = \alpha_{\eta\eta\varsigma}^{(2)}/\alpha_{\varsigma\varsigma\varsigma}^{(2)} = 2.5$. Using eq 2, we can relate $\chi_{sijk}^{(2)}$ to $\alpha_{\rho\rho\rho}^{(2)}$. For an isotropic monolayer, the nonvanishing nonlinear susceptibility elements are

$$\chi_{s,yyz}^{(2)} = \chi_{s,xxz}^{(2)}$$

$$= \frac{3}{8} N L_y(\omega_s) L_y(\omega_{vis}) L_z(\omega_{ir}) [\langle \cos t \rangle (7C_{\eta\eta\varsigma} + C_{\varsigma\varsigma\varsigma}) + \langle \cos 3t \rangle (C_{\eta\eta\varsigma} - C_{\varsigma\varsigma\varsigma})] \alpha_{\rho\rho\rho}^{(2)}$$

$$\chi_{s,zyy}^{(2)} = \chi_{s,zxx}^{(2)}$$
$$= \frac{3}{8} N L_z(\omega_s) L_y(\omega_{vis}) L_y(\omega_{ir}) [\langle \cos t \rangle (-C_{\eta\eta\varsigma} + C_{\varsigma\varsigma\varsigma}) + \langle \cos 3t \rangle (C_{\eta\eta\varsigma} - C_{\varsigma\varsigma\varsigma})] \alpha_{000}^{(2)}$$

$$\begin{split} \chi^{(2)}_{s,yzy} &= \chi^{(2)}_{s,xzx} \\ &= \frac{3}{8} N L_y(\omega_s) L_z(\omega_{vis}) L_y(\omega_{ir}) [\langle \cos t \rangle (-c_{\eta\eta\varsigma} + C_{\varsigma\varsigma\varsigma}) + \\ &\langle \cos 3t \rangle (C_{\eta\eta\varsigma} - C_{\varsigma\varsigma\varsigma})] \alpha^{(2)}_{\rho\rho\rho} \\ \chi^{(2)}_{s,zzz} &= \frac{3}{4} N L_z(\omega_s) L_z(\omega_{vis}) L_z(\omega_{ir}) [\langle \cos t \rangle (C_{\eta\eta\varsigma} + 3C_{\varsigma\varsigma\varsigma}) + \\ &\langle \cos 3t \rangle (-C_{\eta\eta\varsigma} - C_{\varsigma\varsigma\varsigma})] \alpha^{(2)}_{\rho\rho\rho} \end{split}$$

where *t* is the angle between the normal to the water surface *Z* and ζ is the symmetry axis of the methyl group. If the SF, visible, and infrared beams are *s*-, *s*-, and *p*-polarized (*s*, *s*, *p*), respectively, the SF output field is proportional to

$$\chi_{s,ssp}^{(2)} = \chi_{s,yyz}^{(2)} \sin \Theta_{ir}$$
(5)

For the p, p, p polarization combination, the SFG output field is proportional to

$$\chi_{s,ppp}^{(2)} = \chi_{s,zzz}^{(2)} \sin \Theta_s \sin \Theta_{vis} \sin \Theta_{ir} + \chi_{s,zxx}^{(2)} \sin \Theta_s \cos \Theta_{vis} \cos \Theta_{ir} - \chi_{s,xzx}^{(2)} \cos \Theta_s \sin \Theta_{vis} \cos \Theta_{ir} - \chi_{s,xzz}^{(2)} \cos \Theta_s \cos \Theta_{vis} \sin \Theta_{ir}$$
(6)

Here Θ 's refer to the incident angles of the light beams. If $\chi_{s,ssp}^{(2)}$ and $\chi_{s,ppp}^{(2)}$ for the symmetric stretch of CH₃ can be deduced from the SFG measurements for a given beam geometry, then the above equations allow us to determine the orientation of the CH groups, assuming that the orientation distribution is a δ -function.

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(11) In many of the GIXD experiments on amphiphilic molecules we have performed thus far at the undulator beamline BW1, beam damage occurred. The general procedure to reduce X-ray beam damage has been to move the sample continually during the diffraction measurement. X-ray beam damage was corrected for by repeated measurement of a strong standard reflection.

(12) The approximate chain tilt angle T of BrC₂₁OH may be derived from the relation: $\cos T = a_0/a = 5/5.94$ (where a is the unit cell axis and $a_0 = 5$ Å, is the length of the axis for close packed hydrocarbon chains with a zero tilt angle), yielding a value of 32°.

(13) A model structure of $BrC_nH_{2n}OH$, n = 21, 22, was constructed making use of known atomic bond lengths and angles assuming an all-trans conformation. It is already well-established that hydrocarbon chainlike molecules related by glide symmetry forming a layerlike herringbone structure lie with their central chain axes exactly halfway between adjacent glide planes. The refinement thus essentially involves adjustment of the rotation angle of the molecule about its chain axis to get a best fit to the observed Bragg rod data, a procedure described previously.³ A very good match between the calculated and observed Bragg rod intensity profiles of the crystalline monolayers of BrC₂₁OH and BrC₂₂OH proved possible only with use of a partial occupancy of about 0.5 of the Br atom, which may arise from cleavage of the C–Br bond on X-radiation.

(14) Cambridge Structural Database System.

(15) We addressed the question whether monolayers of $BrC_{m-1}COOC_nOH$ behave in an analogous manner to the monolayers of C_mCOOC_nOH with regard to the orientation of the terminal C–X bond (X = CH₃ or Br) exposed to air. According to GIXD measurements on the monolayer of BrC₁₀-COOC₁₀OH, the cell dimensions, chain tilt angle *T* (see entry 6 in Table 3), and thus the packing arrangement remains the same as that of entries 1, 2, 4, 5 listed in Table 3, suggesting that the C–Br bond clearly makes a large polar angle *t* with the layer normal. On the other hand, there is a pronounced change in cell dimensions and increase in chain tilt angle *T* by 12° for BrC₁₁COOC₁₀OH (see entry 7 in Table 3). Thus replacement of the terminal CH₃ group by a Br atom has an effect on the monolayer packing arrangement. This conclusion suggests that the requirement for the C–Br bond to be steeply tilted vis-à-vis the layer normal is more pronounced than for the C–CH₃ bond.

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