



Oriented Crystallization And Nonlinear Optics

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Oriented Crystallization and Non-linear Optics: Tools for Studying Structural Changes of Amphiphilic Aggregates at the Air-solution Interface

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The role played by structured aggregates as intermediates in crystal nucleation is of significant current interest. In a stereochemical approach towards understanding crystal nucleation on a molecular level, we have recently provided evidence that water soluble hydrophobic α -amino acids induce oriented nucleation of α -glycine crystals at air-solution interfaces. These amino acids accumulate at the surface of the solution forming ordered aggregates stabilized by a two-dimensional net of hydrogen bonds similar to their own crystal structure [1]. Such aggregates can induce fast oriented crystallization of suitable co-solute molecules (e.g. glycine) when there is a match between the 2-D molecular arrangement and the structure of the face from which the crystal nucleates.

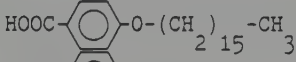
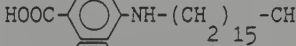
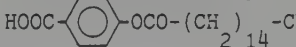
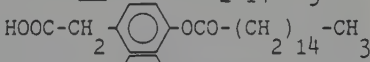
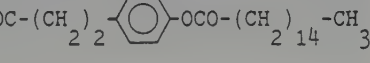
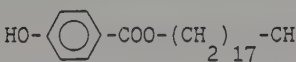
For other types of amphiphiles, it may not be possible to extrapolate a unique 2-D surface structure on the basis of their 3-D crystal structure. In such cases the 2-D structure of these surface aggregates may strongly depend on the nature of the interaction between them and other solute molecules. We demonstrate here profound changes in the structure of monolayers of insoluble 4-substituted benzoic acid amphiphiles upon addition of 4-hydroxybenzoic acid (HBA) to the aqueous subphase. These structural changes have been monitored by two independent processes: the induction of oriented HBA crystals attached to the air-solution interface, and changes in the optical second harmonic generation (SHG) of the monolayer.

Our interest in these systems stems from earlier observations that addition of small amounts of 4-methoxybenzoic acid to crystallizing solutions of HBA

induces fast nucleation of crystal floating at the solution surface [2]. These crystals exhibit a well developed (401) face through which the crystal attaches to the surface. This morphology is very different from that of crystals which grow as {100} plates elongated in the c direction (usually at the bottom of the crystallizing dish) in the absence of the additive.

RESULTS AND DISCUSSION

In order to elucidate the mechanism by which this nucleation occurs, we designed long chain insoluble amphiphilic molecules 1 - 6 with their hydrophilic group the X- ϕ -COOH moiety (X=O,N) to be used in the form of Langmuir films.

No.	Name	Structure
<u>1</u>	4-(hexadecyloxy)benzoic acid	HOOC- 
<u>2</u>	4-(hexadecylamino)benzoic acid	HOOC- 
<u>3</u>	4-(hexadecanoyloxy)benzoic acid	HOOC- 
<u>4</u>	4-(hexadecyloxy)phenylacetic acid	HOOC-CH ₂ - 
<u>5</u>	[4-(hexadecyloxy)phenyl] propionic acid	HOOC-(CH ₂) ₂ - 
<u>6</u>	octadecyl-4-hydroxybenzoate	HO- 

Analogous to the case of the soluble additive, 4-methoxybenzoic acid, (401) oriented nucleation of HBA crystals was also induced at the air-solution interface when amphiphiles 1, 2 or 3 were spread on supersaturated HBA solutions.

However, amphiphilic molecules 4, 5 and 6, of a slightly different structure, did not induce HBA crystallization at the interface.

The different behaviour of the two groups of amphiphiles is also reflected by their π -A isotherms. All the amphiphiles, when compressed over pure water,

form monolayers consisting of molecules oriented almost perpendicular to the surface as determined from the limiting area/molecule (Figure 1), and from the SHG experiments (see below).

When amphiphiles 1, 2, or 3 are compressed over supersaturated solutions of HBA, more expanded π -A isotherms with a larger limiting area/molecule are obtained. In contrast, the limiting area/molecule for 4, 5, and 6 are unchanged.

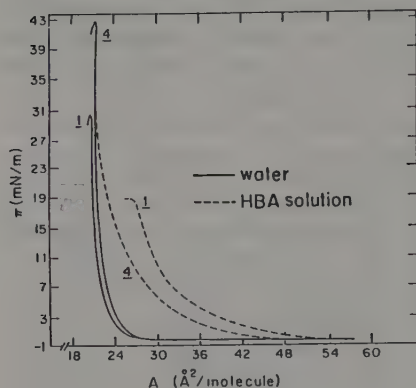


Figure 1 π -A isotherms of amphiphiles spread on water, and on 0.08M HBA solution. Isotherms for compounds 2, 3 are similar to 1 and that of 5 and 6 are similar to 4.

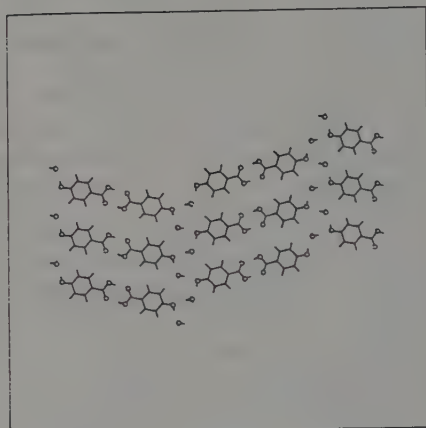


Figure 2 Packing arrangement of 4-hydroxybenzoic acid monohydrate crystal viewed perpendicular to the (401) face.

These results suggested the following mechanism: In the crystal structure [3] of the 4-hydroxybenzoic acid monohydrate (space group $P2_1/a$), the HBA molecules lie parallel to the (401) plane, forming hydrogen-bonded dimers (Figure 2). These dimers are interlinked within the (401) plane by hydrogen bonds involving the phenolic -OH groups and water molecules. The induced crystallization of HBA at the air-solution interface suggests that amphiphiles 1, 2, 3 form aggregates whose structure mimics that of the (401) crystalline face. This model implies that the 4-oxybenzoic acid moieties lie flat on the surface such as to form the hydrogen-bonded dimers, while their aliphatic chains emerge from the solution (Figures 3 and 4). A photograph of actual

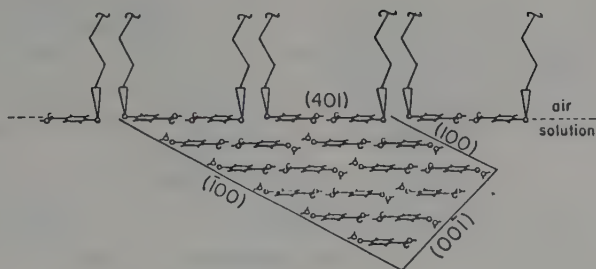


Figure 3 Packing arrangement HBA crystal with the (401) face viewed 'edge-on', delineated by the crystal faces. The layer of molecules at the interface is the Langmuir film (represented schematically).

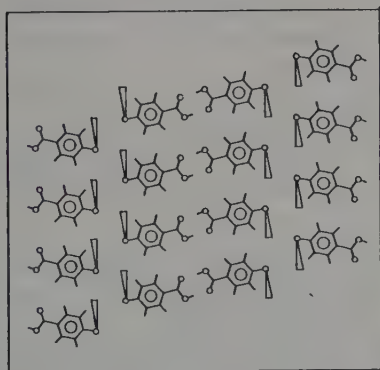


Figure 4 (left) Proposed amphiphile structure viewed perpendicular to the HBA subphase. The O(phenol)...O(phenol) distance between adjacent molecules is 4.6 Å, allowing good van der Waals contacts between chains.

Figure 5 (right) Photograph of HBA crystals.



HBA crystals grown attached to these amphiphiles is shown in Figure 5.

In order to independently verify that the specified amphiphiles change their orientation when HBA is added to the aqueous subphase we have studied these systems with second harmonic generation (SHG). This is a surface specific technique [4] which can determine the presence and orientation of surface adsorbates on centrosymmetric and isotropic substrates. Our experimental system for SHG is depicted in Figure 6.

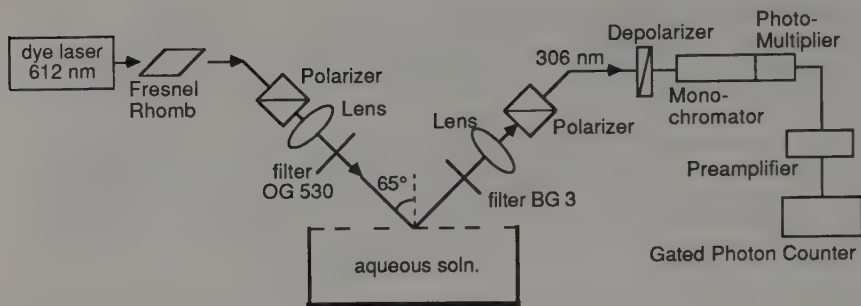


Figure 6 SHG experimental set-up. The dye laser, pumped at 10Hz by a Nd-YAG laser, produces 8ns pulses of energy 5mJ. SHG signals are typically averaged over 2000 pulses.

The second order polarization, $P^{(2)}$, induced in a medium by an optical electric field, $E(\omega)$, is described by the nonlinear susceptibility tensor, $\chi^{(2)}$

$$P_i^{(2)} = \chi_{ijk}^{(2)} E_j(\omega) E_k(\omega) \quad (1)$$

It is readily seen from this equation that in a centrosymmetric medium $\chi_{ijk}^{(2)} = 0$, and thus dipole allowed SHG can only arise from the surface where the symmetry is broken.

The orientation of the major nonlinear optical axis (here the long axis of the phenyl group) of the amphiphile relative to the surface normal (θ) can be determined from the surface $\chi^{(2)}$ tensor. For a rod-like molecule whose azimuthal distribution in the surface plane is isotropic, there are only 2 independent $\chi^{(2)}$ components [4]:

$$\chi_{zzz}^{(2)} = N_s \beta \langle \cos^3 \theta \rangle \quad (2)$$

$$\chi_{yzy}^{(2)} = \chi_{zyy}^{(2)} = \chi_{zxx}^{(2)} = \chi_{zzx}^{(2)} = 1/2 N_s \beta \langle \sin^2 \theta \cos \theta \rangle$$

Here N_s is the number of monolayer molecules per unit surface area, and β is the second order nonlinearity per molecule.

The s- and p- polarized SHG signals generated by a 45° polarized input laser (I_{45-s} and I_{45-p} respectively) are related to the $\chi^{(2)}$ coefficients:

$$[I_{45-s}]^{1/2} \sim a_1 \chi_{yzy}^{(2)}$$

$$[I_{45-p}]^{1/2} \sim a_2 \chi_{yzy}^{(2)} + a_3 \chi_{zzz}^{(2)} \quad (3)$$

The α coefficients are evaluated [5] assuming a value of 1.5 for the refractive indices of the organic monolayer. Assuming a narrow distribution of θ values within the monolayer, $\langle\theta\rangle$ may be evaluated from the ratio of I_{45-s} to I_{45-p} . Magnitudes of β were evaluated from the ratio of amphiphile SHG to that of the bare water surface, for which $\chi_{yzy} = 2 \times 10^{-17}$ e.s.u. [6].

Amphiphiles 1, 2 and 6 spread on water all exhibited SHG signals considerably stronger than that of the bare water subphase, and $\langle\theta\rangle$ values in the range $24^\circ - 47^\circ$ (Table 1). These $\langle\theta\rangle$ values refer to the orientation of the polar $\text{XC}_6\text{H}_4\text{COO}$ head group, but not necessarily to the orientation of the hydrocarbon chain.

Table 1 SHG signals and orientations for monolayers on water and saturated HBA solution.

Monolayer	ON WATER				ON HBA		
	I_{45-s}	I_{45-p}	$\theta(^{\circ})$	$\beta(\text{esu})$	I_{45-s}	I_{45-p}	$\theta(^{\circ})$
Bare Subphase	1	0.6			0.4	0.8	
<u>1</u>	10	40	24	2×10^{-30}	same as subphase		90
<u>1</u> 80% cov.	7	30	24	2×10^{-30}	7	30	24
<u>2</u>	450	150	42	7×10^{-30}	same as subphase		90
<u>6</u>	150	40	47	3×10^{-30}	150	40	47

The bare HBA subphase had an SHG intensity similar to that of water. Whereas the SHG signal and $\langle\theta\rangle$ of 6 on HBA solution were the same as on water, the SHG of full monolayers of 1 and 2 on HBA were very different. The total SHG signal in these two cases was about the same as that of the bare HBA solution. This is entirely consistent with our model since the lack of SHG from the compounds 1 and 2 means, according to equation (2), that their polar moiety $\text{XC}_6\text{H}_4\text{COOH}$ lies flat ($\theta = 90^\circ$) on the HBA solution surface.

The absence of SHG signals from these monolayers on HBA could in principle arise from another reason - the formation of a bilayer (at any angle to the surface) between one HBA molecule from the solution and an amphiphile molecule, leading to a cancellation of

their nonlinearities. This might be possible (at least in principle) for the monolayer of 1 but can be discounted for 2 due to the large difference in β values of the 4-hydroxybenzoic and 4-aminobenzoic chromophores. Thus the SHG results can only be explained by monolayers of 1 and 2 lying flat ($\theta = 90^\circ$) on the water surface.

At 80% of the full monolayer coverage, the $\langle\theta\rangle$ value of 1 spread on HBA is the same as on water, implying that its interaction with solute molecules at this coverage density is insufficient to change the orientation.

The fact that the HBA subphase can drastically alter the surface alignment of monolayers of 1 and 2 but not the closely related monolayer of 6 demonstrates how specific the solute-amphiphile interactions can be. We have further demonstrated this by checking the SHG of 1 spread on an aqueous solution of 4-hydroxy-phenylacetic acid (i.e. the addition of one methyl group to the HBA molecule). Over this solution, the monolayer of 1 shows exactly the same SHG signal strength and $\langle\theta\rangle$ value (24°) as on pure water, indicating the loss of the strong solute/amphiphile interaction with the small change in the solute molecule, in perfect agreement with the π -A isotherm and crystallization experiments.

In conclusion, our combination of several independent techniques, namely oriented crystallization, surface pressure-area isotherms and second harmonic generation, presents a very powerful approach for studying the structures of surface aggregates, and their interactions with solute molecules in the subphase.

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