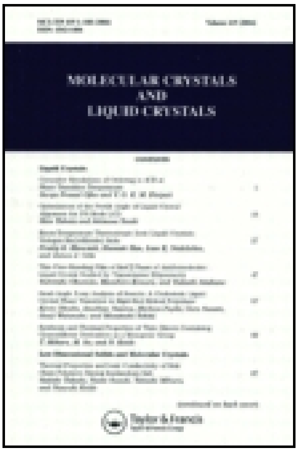

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

SEARS: Clathrates of Dianin's Compound: An Inelastic Neutron Scattering Investigation

G. Berkovic [a] & I. Weissbuch [a]
[a] Department of Structural Chemistry, Weizmann Institute of Science, Rehovot, Israel, 76100

Version of record first published: 27 Oct 2006.

To cite this article: G. Berkovic & I. Weissbuch (1992): SEARS: Clathrates of Dianin's Compound: An Inelastic Neutron Scattering Investigation, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 211:1, 183-188

To link to this article: http://dx.doi.org/10.1080/10587259208025818

Mol. Cryst. Liq. Cryst. 1992, Vol. 211, pp. 183–188
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

SECOND HARMONIC GENERATION STUDIES OF MONOLAYERS: ORIENTATIONS, SURFACE COVERAGES AND INTERACTIONS

G. BERKOVIC AND I. WEISSBUCH
Department of Structural Chemistry, Weizmann Institute of Science,
Rehovot, Israel 76100

(Received July 12, 1991)

Abstract Aggregation of cinnamic acid and cinnamamide derivatives is studied at the air/aqueous interface. We study both the spontaneous surface aggregation of soluble molecules from their aqueous solution, and insoluble monolayers of long alkyl chain derivatives on various subphases. The interaction at the surface between soluble and insoluble species is also probed.

Keywords: monolayers, second harmonic generation

INTRODUCTION

It has been known since the pioneering work of Gibbs and Langmuir that soluble and insoluble amphiphilic organic molecules can respectively aggregate and form monolayers at the surface of aqueous solutions. In recent years there has been a resurgence of interest in these systems, as a basis for the preparation of organized structures,[1] specialized surface coatings,[2] and induced preferential crystallizations.[3]

In parallel, new surface sensitive experimental techniques have been developed[4,5] to provide a more quantitative picture of the surface interactions and structures in these type of systems. Here, we use the nonlinear optical technique of surface second harmonic generation (SHG) to probe[6-8] soluble and insoluble monolayers, and the interactions between them, at the air/aqueous interface.

Recently, we reported[9] a study of systems in which insoluble amphiphiles are spread as monolayers on a saturated solution of 4-hydroxybenzoic acid (HBA). In the bare aqueous solution, this solute does not aggregate significantly at the surface; however, spreading a suitable insoluble monolayer at the surface induced a surface structure consisting of a bilayer of the insoluble amphiphile and HBA. In this bilayer, the aromatic rings of both species lie flat on the water surface, in stark contrast to the equilibrium monolayer structure of the insoluble molecule spread on pure water. This structured aggregate, which mimics the HBA (401) crystal face, provides the template for induced crystallization of HBA attached by this face to the surface.

In the present work we describe the surface interactions of derivatives of p-substituted cinnamic acids and amides. Molecules with short chain substituent groups are soluble, but their hydrophobic character causes spontaneous aggregation at the surface of their aqueous solutions. Long chain hydrocarbon substituent groups render the molecules insoluble, forming good Langmuir type monolayers.

EXPERIMENTAL

The materials used in this study are shown in Figure 1. 4-Methoxy cinnamic acid (MCA) and 4-methoxy cinnamamide (MCAM) are somewhat soluble in water, and are prepared as 4-6 x 10^{-4} M aqueous solutions. The long chain octadecyloxy derivatives ODCA and ODCAM are insoluble in water, but can be spread from chloroform solution to form Langmuir type monolayers on water.

SOLUBLE MOLECULES

4-Methoxy cinnamic acid (MCA) **4-Methoxy cinnamamide (MCAM)**

INSOLUBLE MOLECULES

4-Octadecyloxy cinnamic acid (ODCA) **4-Octadecyloxy cinnamamide (ODCAM)**

Figure 1

Measurements of the SHG from the air/solution interface were performed as described in detail previously.[10] The laser source for the measurements is a pulsed dye laser operating at 612nm, and providing pulses of duration 6ns and energy 5mJ. The orientation of the long molecular axis of monolayer molecules at the interface can be calculated from the ratio of SHG signals in two independent polarization combinations - thus we measure the SHG intensities I(45-s) and I(45-p) which are the s- and p-polarized SHG intensities generated by input light of 45° polarization. Signal intensities are expressed relative to that of the pure water subphase, of known surface nonlinear susceptibility, and thus the nonlinearity per monolayer molecule may be estimated.

RESULTS AND DISCUSSION

The surface SHG intensities have been measured for

(i) the two insoluble long chain molecules ODCA and ODCAM as full monolayers (approx 4×10^{14} molecules/cm^2, determined independently from π-area isotherms)
(ii) saturated solutions of the two soluble molecules MCA and MCAM
(iii) monolayers of the insoluble molecules spread on saturated solutions of the soluble molecules.

Results are presented in Table 1. The average orientation of the molecular long axes to the surface normal, $\langle\theta\rangle$, and the average nonlinearity per molecule, β, are calculated from the data as described previously.[10] For the experiments of categories (ii) and (iii) we may express the total surface nonlinearity as

$$\Sigma N\beta = N_i\beta_i \pm N_s\beta_s$$

where the i and s subscripts refer to the insoluble and soluble molecules, and N is the number of molecules per unit surface area. The ± signs refer to the cases where the soluble and insoluble species point in the same or opposite directions respectively. If we make the reasonable assumption that $\beta_i = \beta_s$, we may deduce N_s, which is consequently normalized to the full monolayer coverage (4×10^{14} molecules/cm^2) to give ϕ_s, the fractional surface coverage of soluble molecules.

The results of the surface SHG of the pure solutions of soluble molecules MCA and MCAM [set (ii)] show that these molecules spontaneously aggregate at the surface, to the extent of 40-45% of the equivalent full monolayer coverage. The molecular long axis is slightly more tilted from the normal than for full monolayers of the corresponding insoluble molecules. It should be pointed out that these results could be consistent with a net coverage of $\approx$ 40% in a single layer at the surface, or spread over a small thickness in the "near surface" region.

	subphase	insol ML	I(45-s)	I(45-p)	$<\theta>$	$\Sigma N\beta$	ϕ_S
(i)	water	ODCA	70	100	29°	$2\mathrm{x}10^{-15}$	
	water	ODCAM	40	100	25°	$2\mathrm{x}10^{-15}$	
(ii)	MCA	none	40	20	41°	$9\mathrm{x}10^{-16}$	45%
	MCAM	none	30	15	41°	$8\mathrm{x}10^{-16}$	40%
(iii)	MCA	ODCA	20	8	40°	$7\mathrm{x}10^{-16}$	65%
	MCA	ODCAM	16	8	40°	$6\mathrm{x}10^{-16}$	70%
	MCAM	ODCAM	18	11	36°	$7\mathrm{x}10^{-16}$	65%
	MCAM	ODCA	9	4	39°	$5\mathrm{x}10^{-16}$	75%

TABLE 1. The SHG intensities obtained from the surfaces of various subphases (water and saturated solutions of MCA and MCAM) covered by insoluble monolayers. I(45-s) and I(45-p) have uncertainties ±30%, and are normalized to the I(45-s) signal of pure water. $<\theta>$ values are ±4°. $N\beta$ is in units of esu, and thus we deduce that for both ODCA and ODCAM $\beta = 5\mathrm{x}10^{-30}$ esu/molecule.

In all the experiments of set (iii) where an insoluble monolayer is spread on a solution, we find the total SHG is less than either the soluble or insoluble species alone. This may be explained by a physically reasonable structure in which the acid or amide head group of the insoluble species, which points down into the solution, interacts with the corresponding group of the soluble species, forming a hydrogen-bonded quasi-centrosymmetric dimer. Therefore, equating $\Sigma N\beta$ with $N_i\beta_i - N_S\beta_S$ we calculate ϕ_S, finding somewhat higher coverages than those of the bare solutions. It appears that the ϕ_S values for the acid-amide pairs are slightly higher than those of the "like" pairs, although the differences are of the same order as the experimental uncertainty.

These measurements provide a direct proof of the strong interactions between the soluble and insoluble molecules, which we ascribe to formation of hydrogen bonding between the two species. Similar conclusions were inferred[11] from X-ray reflectivity measurements of glutamine solute molecules attached below an amino acid amphiphile.

We may also ask what is the structure of MCA and MCAM molecules at the surface of their pure solutions. The SHG intensities alone cannot distinguish which end of the molecule points out of the water. However, we may determine this by a relative SHG phase measurement.[12] This is performed by placing a quartz crystal in the path of the SHG (and residual fundamental) reflected from the aqueous interface.The harmonic waves generated by the interface and by quartz will add either constructively or destructively depending on the relative phase between them. By varying this phase difference (with the assistance of a small variable pressure cell inserted between them) we can measure a SHG interferogram. In Figure 3 we show interferograms produced by the ODCA monolayer on pure water, and by the bare solution of MCA. The interferograms are identical, meaning that the SHG of MCA and ODCA are in phase. Since the acid head group of ODCA must point down into the water, we therefore conclude that the surface MCA molecules have their methoxy groups pointing out of the aqueous phase, and the acid group pointing down. In a similar way, we also showed that the amide group of MCAM also points down into the water.

Thus these measurements imply that when corresponding long chain molecular monolayers are spread over aqueous solutions of MCA and MCAM, solute molecules are attached to the surface with their carboxylic acid groups pointing in the opposite

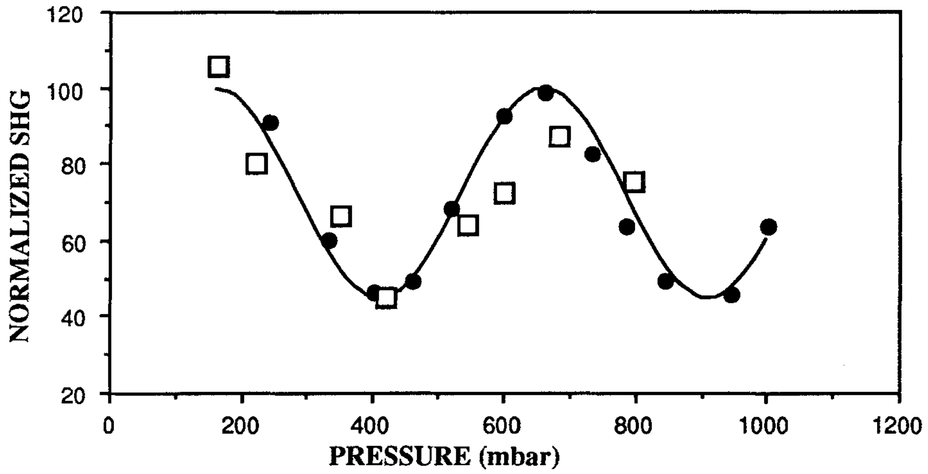

Figure 2. SHG interferograms measured when the SHG from bare MCA solution (circles) or from ODCA monolayer on water (squares) is combined with the SHG generated by a quartz crystal, whereby a 4.5 cm long cell of variable air pressure is placed between the two SHG sources. SHG intensities are normalized to the maximum signal of each experiment. The full curve represents a theoretical fit, whose periodicity is defined by the extra optical phase difference between 612nm and 306nm induced by the cell.

direction to that found in the bare solution (see Figure 3). Thus the acid-acid and amide-acid interactions are sufficiently favourable energetically to overcome the preference of the spontaneously organized molecules.

In conclusion, these measurements have shown and quantified the spontaneous surface aggregation of soluble cinnamic acid/amide derivatives from their aqueous solutions, and the change in orientation upon strong interaction with monolayers of insoluble analogues.

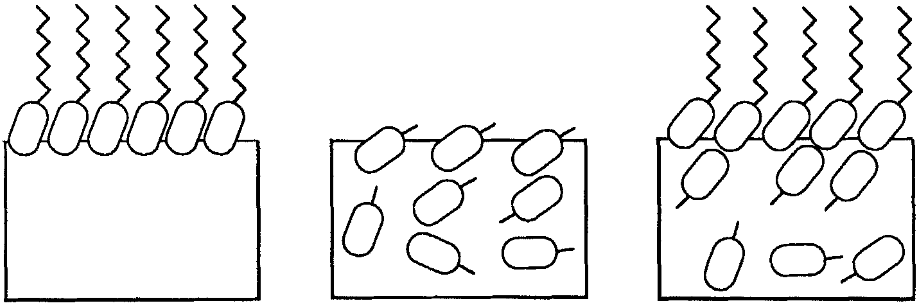

Figure 3. Proposed model for cinnamic acid and cinnamamide monolayers at the air/aqueous interface as deduced from SHG measurements. Note that this only provides structural information about the polar head groups - the structure of the tail is assumed.

REFERENCES

1. J.D. Swalen, D.L. Allara, J.D. Andrade, E.A. Chandross, S. Garoff, J. Israelachvili, T.J. McCarthy, R. Murray, R.F. Pease, J.F. Rabolt, K.J. Wynne and H. Yu, Langmuir 3, 932 (1987).
2. E.B. Troughton, C.D. Bain, G.M. Whitesides, R.G. Nuzzo, D.L. Allara and M.D. Porter, Langmuir 4, 365 (1988).
3. E.M. Landau, S. Grayer Wolf, M. Levanon, L. Leiserowitz, M. Lahav and J. Sagiv, J. Am. Chem. Soc. 111, 1436 (1989).
4. D. Jacquemain, S. Grayer Wolf, F. Leveiller, M. Deutsch, K. Kjaer, J. Als-Nielsen, M. Lahav and L. Leiserowitz, Ang. Chem. Int. Ed. Eng. in press.
5. R.M. Weis and H.M. McConnell, Nature 310, 47 (1984).
6. J.M. Hicks, K. Kemnitz, K.B. Eisenthal and T.F. Heinz, J. Phys. Chem. 90, 560 (1986).
7. X. Zhao, M.C. Goh and K.B. Eisenthal, J. Phys. Chem. 94, 2222 (1990).
8. X.D. Xiao, V. Vogel and Y.R. Shen, Chem. Phys. Lett. 163, 555 (1989).
9. I. Weissbuch, G. Berkovic, L. Leiserowitz and M. Lahav, J. Am. Chem. Soc. 112, 5874 (1990).
10. G. Berkovic, Physica. A 168, 160 (1986).
11. S. Grayer Wolf, E.M. Landau, M. Lahav, L. Leiserowitz, M. Deutsch, K. Kjaer and J. Als-Nielson, Thin Solid Films 159, 29 (1988).
12. R.K. Chang, J. Ducuing and N. Bloembergen, Phys.Rev. Lett. 15, 6 (1965).