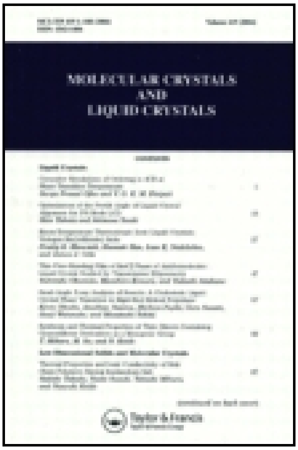


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Langmuir Monolayers Designed for the Oriented Growth of Glycine and Sodium Chloride Crystals at Air/Water Interfaces

Ehud M. Landau [a], Ronit Popovitz-biro [a], Moshe Levanon [a], Leslie Leiserowitz [a], Meir Lahav [a] & Jacob Sagiv [a]

[a] Departments of Structural Chemistry+, and Isotope Research* Weizmann Institute of Science, Rehovot, 76100, Israel

Version of record first published: 17 Oct 2011.

To cite this article: Ehud M. Landau, Ronit Popovitz-biro, Moshe Levanon, Leslie Leiserowitz, Meir Lahav & Jacob Sagiv (1986): Langmuir Monolayers Designed for the Oriented Growth of Glycine and Sodium Chloride Crystals at Air/Water Interfaces, Molecular Crystals and Liquid Crystals, 134:1, 323-335

To link to this article: http://dx.doi.org/10.1080/00268948608079593

Mol. Cryst. Liq. Cryst., 1986, Vol. 134, pp. 323-335
0026-8941/86/1344-0323$20.00/0

Printed in the United States of America

LANGMUIR MONOLAYERS DESIGNED FOR THE ORIENTED GROWTH OF GLYCINE AND SODIUM CHLORIDE CRYSTALS AT AIR/WATER INTERFACES

Ehud M. Landau,[+] Ronit Popovitz-Biro,[+] Moshe Levanon,[+]
Leslie Leiserowitz,[+] Meir Lahav[+] and Jacob Sagiv[*].

Departments of Structural Chemistry[+] and Isotope Research[*]
Weizmann Institute of Science, Rehovot 76100, Israel

Abstract: Oriented growth of crystals of α-glycine and sodium chloride under compressed Langmuir monolayers at air-water interfaces was achieved. For α-glycine, a variety of monolayers containing resolved glycyl head groups and different hydrophobic moieties were used, thus establishing the structural requirements necessary for oriented crystallization. For sodium chloride, monolayers of positive, negative and zwitterionic charge induced crystal nucleation from faces of the type {100}, {110} and {111}, the latter two faces not being naturally occurring.

INTRODUCTION

Oriented crystallization of three-dimensional crystals under compressed Langmuir monolayers at an air-solution interface is governed by a favourable interaction between the hydrophilic moieties of the monolayer molecules and the first layer of the attached nucleating crystal.[1] Under auspicious conditions a compressed monolayer may be designed so that the arrangement of its polar head groups simulate a layer of a given crystal, thus triggering nucleation from that layer. In the absence of such a perfect structural fit, the aim would be to engineer a specific interaction with a given set of atoms within a layer of the crystal, thus inducing nucleation. The possibility of controlling the packing arrangements of the polar head groups by chemical modification of the hydrophobic side chains provides a simple approach for the systematic investigation of the structural requirements for nucleation. In the present study we have followed these approaches by investigating the oriented crystal growth of glycine and sodium chloride in aqueous solutions starting from monolayers.

GLYCINE

Glycine crystallizes from aqueous solution in the α-form (space group $P2_1/n$), exhibiting a bipyramidal habit.[2] The glycine molecules form hydrogen-bonded chiral layers parallel to the ac plane[3] (Fig.1A). These glycine layers are juxtaposed on one side of the b axis by centres of inversion, about which the molecules are interlinked by N-H···O bonds to form centrosymmetric hydrogen-bonded bilayers (Fig.1B). These bilayers are related by twofold screw symmetry to complete the crystal packing (Fig.1C). The requirements for a monolayer to completely simulate the first ac chiral layer of glycine at the air-water interface are: (a) The surfactant molecules should incorporate resolved α-amino acid head groups (Figs.1B,1D). (b) The hydrophobic moieties of the monolayer-forming molecules should not hinder the neighbouring glycyl head groups from packing in a layer arrangement very similar to that of α-glycine (Fig.1A).

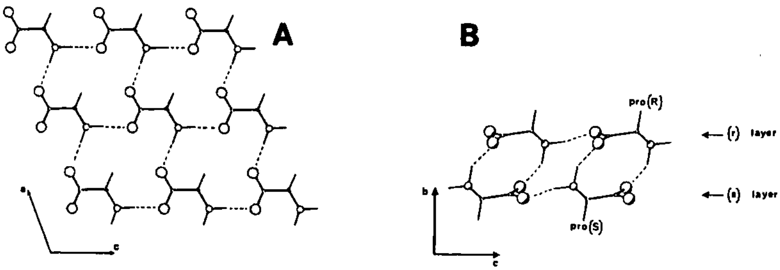


Figure 1

(A) An ac layer of hydrogen-bonded glycine molecules viewed along the b-axis. The layer is defined as r since the H atoms of the C-H bonds which emerge from the ac plane are pro (R);

(B) A centrosymmetric bilayer of hydrogen-bonded glycine molecules viewed perpendicular to the bc plane. The upper r layer is that shown in (A);

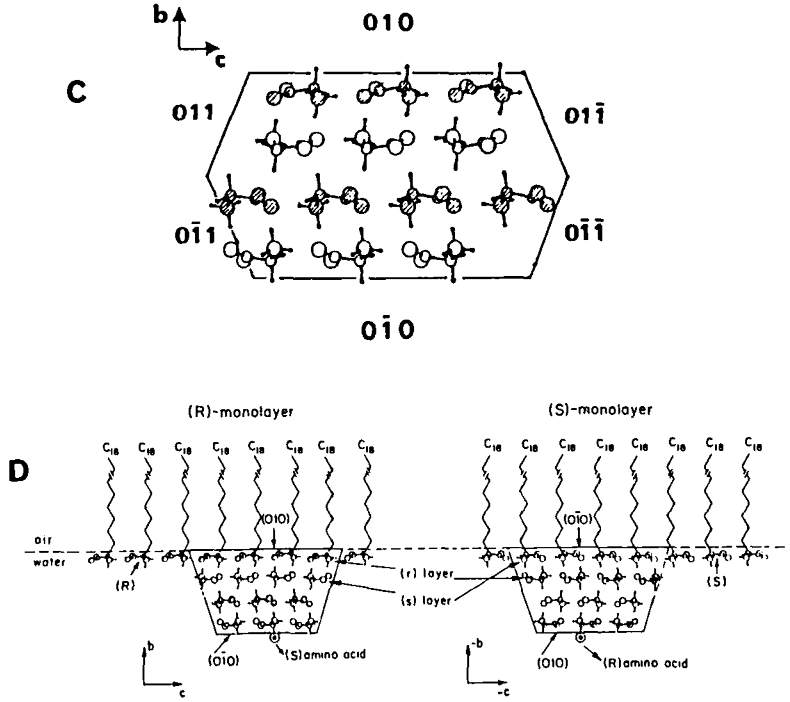


Figure 1

(C) Packing arrangement of α-glycine, delineated by its crystal faces. The bilayers (B) are related by 2-fold screw symmetry along the $\underline{b}$ axis;

(D) Schematic views of pyramidal crystals of glycine grown under compressed (R) and (S) amino acid monolayers. The (010) face of glycine is attached to the (R) monolayer and the $(0\bar{1}0)$ face to the (S) monolayer. (S) and (R) amino acids are shown adsorbed from solution at the $(0\bar{1}0)$ and (010) faces respectively.

Langmuir monolayers comprising amphiphilic α-amino acids induce oriented growth of crystals of α-glycine, by virtue of a structural match between the monolayer and the *ac* surface layer of the growing glycine crystals. Table 1 summarizes the experimental results.

TABLE I Crystallization data of α-glycine under compressed monolayers at the air-water interface:‡
(a) limiting area per molecule (Å^2);
(b) degree of[*] orientation (%) and face exposed to the monolayer ; (c) rate of crystallization.

	Monolayer	(a)	(b)	(c)
1.	(R)$CH_3(CH_2)_{15}CH(NH_3^+)CO_2^-$	25	93, (010)	Fast
	(S)$CH_3(CH_2)_{15}CH(NH_3^+)CO_2^-$	25	91, (0$\bar{1}$0)	Fast
	(R,S)$CH_3(CH_2)_{15}CH(NH_3^+)CO_2^-$	25	~ 50, (010) ~ 50, (0$\bar{1}$0)	Fast
2.	(R)$CH_3(CH_2)_{17}OOOCH_2CH(NH_3^+)CO_2^-$	29	> 99, (010)	Fast
	(S)$CH_3(CH_2)_{17}OOOCH_2CH(NH_3^+)CO_2^-$	29	> 99, (0$\bar{1}$0)	Fast
3.	(R)$CH_3(CH_2)_{17}OOO(CH_2)_2CH(NH_3^+)CO_2^-$	29	> 99, (010)	Fast
	(S)$CH_3(CH_2)_{17}OOO(CH_2)_2CH(NH_3^+)CO_2^-$	29	> 99, (0$\bar{1}$0)	Fast
4.	(S)$CF_3(CF_2)_9(CH_2)_2OOOCH_2CH(NH_3^+)CO_2^-$	—	65–75, (0$\bar{1}$0)	Fast
5.	(S) 5-α-Cholestan-3β-OOOCH$_2$CH(NH$_3^+$)CO$_2^-$	38	No orientation	Slow

‡ All crystallization experiments were performed at 20±2°C by compressing the monolayers to their limiting areas per molecule over 4.66 M aqueous solutions of glycine. The monolayer area was kept constant during crystallization.

---

[*] The degree of orientation is defined as the percentage of crystals exposing attached face (010) or (0$\bar{1}$0) to the monolayer, depending upon whether the monolayer is composed of (R) or (S) molecules respectively.

Condensed monolayers of compounds 1-3, measured over pure water, exhibit limiting areas per molecule in the range of 25-29 Å^2 (Fig.2). These values straddle the molecular unit surface area of 25.6 Å^2 of an ac layer (i.e. ac sinβ) of glycine molecules in its crystal structure. These monolayers induced immediate nucleation of pyramidal glycine crystals, with their ac faces attached to the monolayer. Most crystals exposed their (010) faces to monolayers of the (R)-α-amino acids and, by symmetry, enantiomorphous pyramids were observed exposing their $(0\bar{1}0)$ faces to monolayers of the (S)-α-amino acids. Monolayers of racemic composition yielded attached crystals of both types.

Monolayer of compound 5, containing the cholestanoyl moiety, has a limiting area per molecule which is determined by the bulky steroid skeleton. It was measured to be 38Å^2 (Fig.2), a value distinctly larger than that of the glycyl head group, thus precluding hydrogen bonding between the latter. Indeed glycine was observed to crystallize at a much slower rate than with monolayers 1-3, exhibiting both pyramidal and bipyramidal morphologies with no preferential orientation.

The behaviour of the monolayer of the perfluoro compound 4 is less clear to interpret due to experimental difficulties in determining the limiting area per molecule.[1] We might expect, assuming a limiting molecular surface area of the order of 30Å^2 (Fig.2)[5,6], that the glycyl head groups would form a hydrogen-bonded layer, but with longer H-bonding distances than in the corresponding hydrocarbon monolayers. Monolayers of compound 4 induced immediate crystallization of glycine, but with a much lower degree of orientation, 65-75%, than in the case of monolayers 1-3. In conclusion, the three distinct modes of crystallization under the monolayers, fast oriented, fast unoriented and slow unoriented, imply a very sensitive dependence of the crystallization process on small changes in the structure of the monolayer.

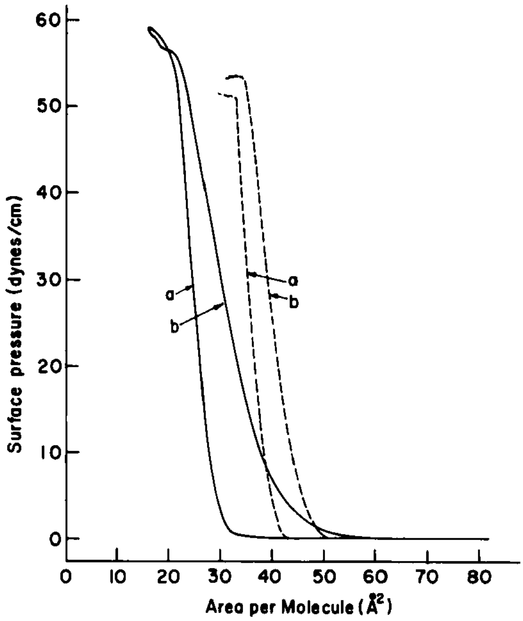


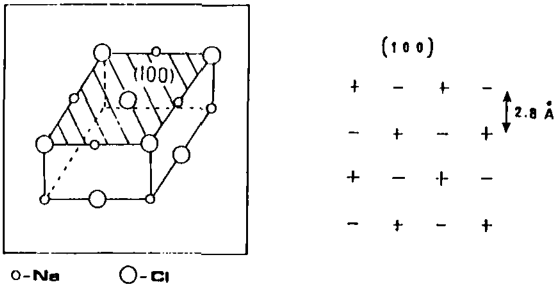
Fig.2 Surface pressure-area isotherms measured at 20±2°C on (a) pure water and (b) 2.66 M aqueous solution of glycine: (——) compound 2 (S); (---) compound 5. The monolayers were spread from solutions in hexane (96%) and trifluoroacetic acid (4%).

SODIUM CHLORIDE

Crystallization of sodium chloride is less specific than glycine since the structure of the monolayer cannot simulate the first layer of the crystal. However nucleation may be induced from different faces via electrostatic interaction with a given set of ions within a layer of the face. Monolayers may be designed to stabilize faces which are not naturally occurring and so induce oriented crystal growth therefrom.

Sodium chloride crystallizes from aqueous solution in the cubic space group $\underline{Fm\bar{3}m}$, $\underline{a}$=5.638Å, exhibiting the {100} faces. Under certain conditions, the two other, less stable sets of faces, {110} and {111} can also develop.[4] By using different monolayers containing head groups of positive, negative or zwitterionic charge attached to a variety of hydrophobic moieties, we may expect to stabilize the different types of NaCl faces and thus establish a correlation between the structure and charge distribution of a given monolayer and a specific face of sodium chloride. Sodium chloride was crystallized under monolayers with various types of polar head groups and the faces nucleated under each monolayer were assigned by X-ray diffraction.

Crystallization of sodium chloride under a monolayer of octadecylamine led to the formation of plate like crystals (Fig.3.) with the {100} face attached to the monolayer. The positive and negative ions are evenly distributed in this face (Scheme $\underline{1}$), which hints to a similar arrangement in the monolayer. The limiting molecular surface area of 31.0Å^2 measured for octadecylamine over a 6M aqueous solution of sodium chloride suggests that the chloride ions penetrate between the octadecyl ammonium molecules. This area is almost equal to the repeat surface area of NaCl of 31.8Å^2.



Scheme 1

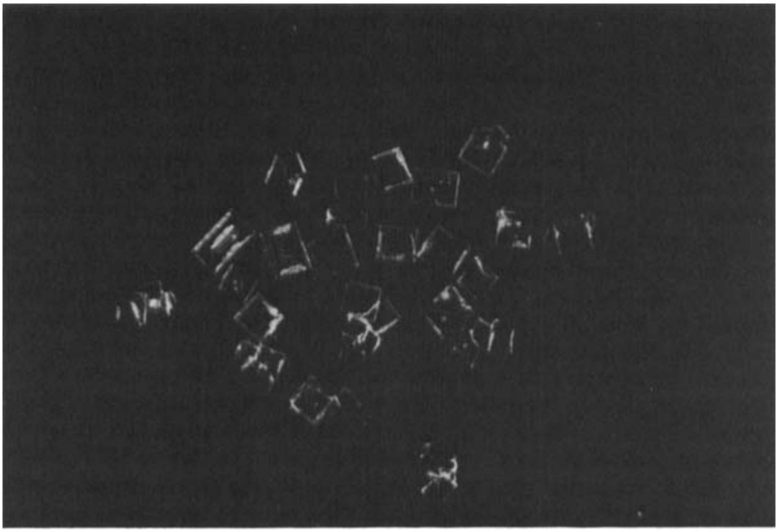
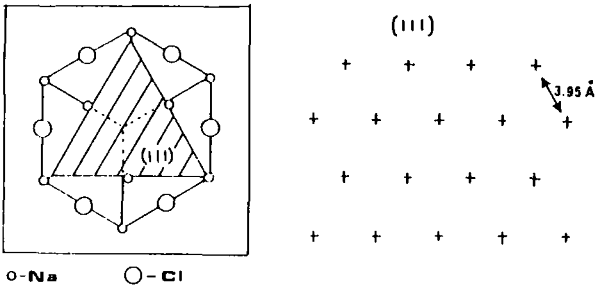


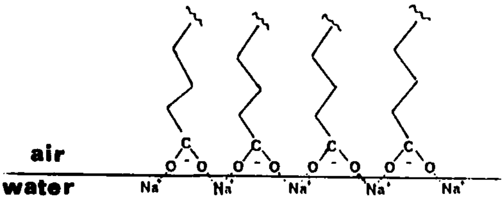
Fig.3 Crystals of sodium chloride grown under a monolayer of octadecylamine from a 6M solution (x6).

When monolayers of various carboxylic acids like stearic or arachidic acid were spread over a solution of sodium chloride, 70-90% of the crystals nucleated under the monolayer were attached with their {111} face (Fig.4). The {111} face is comprised of ions of one type only as shown in Scheme 2.



Scheme 2

Nucleation from the {111} face may be induced by concentration of sodium ions in a layer under the compressed carboxylate moieties, without having the possibility of penetration in between the molecules of the monolayer, as shown in Scheme 3. When the hydrophobic chain was changed to a bulkier group by using a styrene or a diacetylene moiety, the percentage of modified crystals was reduced to 15 and 40% respectively and when a monolayer of cholesteryl succinate was used, in which the carboxylic groups were further separated by the bulky steroid, no nucleation under the monolayer was observed.



Scheme 3

A monolayer of stearoyl-R-glutamate caused nucleation of 70–80% of the sodium chloride crystals from the {110} face (Fig.5) at pH 1-3; at pH 4-6 the percentage of crystals with the {110} face attached to the monolayer dropped to 40-50% and the {111} modification started to appear.

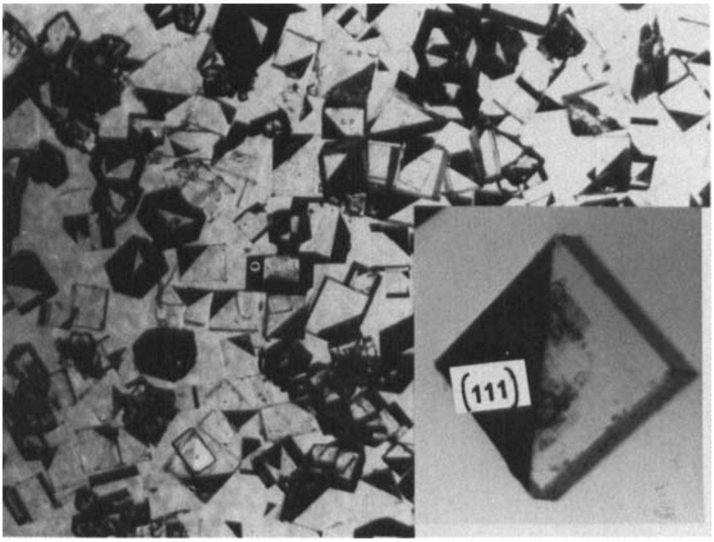
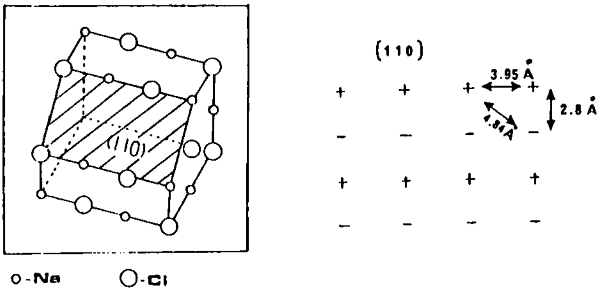


Fig.4 Crystals of sodium chloride grown under a monolayer of stearic acid from a 6M solution. (x12). (Insert x50).

The arrangements of ions in the {110} face is shown in Scheme 4. In this face the ions are arranged in rows of opposite charge. The positive and negative charges are evenly distributed but in an energetically less favourable arrangement than in the {100} face. Stabilization of such a face suggests oriented growth from a monolayer composed of rows of alternating charges.



Scheme 4

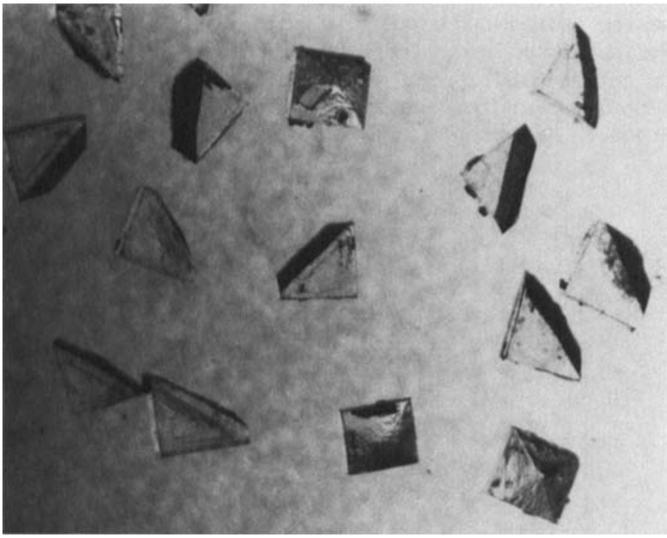


Fig.5 Crystals of sodium chloride grown under a monolayer of stearoyl-R-glutamate from a 6M solution at pH 3. (x15).

DISCUSSION

These preliminary studies have demonstrated that compressed Langmuir monolayers may serve as most efficient nucleators for the oriented growth of organic and inorganic crystals at the air-solution interface. Our results suggest that the rate of nucleation and the face from which a given crystal starts growing at the monolayer interface strongly depend both on the chemical nature and on the arrangement of the hydrophilic head groups in the water layer. The packing of these head groups may be modified by changing the cross-section of the hydrophobic moieties.

In order to understand the nucleation process, a clear picture of the structure of the monolayer and adjacent liquid layer prior to crystallization is required, as well as the molecular arrangement of the monolayer attached to the crystal face. Several approaches are being undertaken to achieve this aim, primarily by the recently developed technique of grazing angle X-ray diffraction using a synchrotron light source. A wider application of oriented crystallization is being undertaken by using solid supports coated by Langmuir-Blodgett films, the results of which will be reported elsewhere.

REFERENCES

1. E.M. Landau, M. Levanon, L. Leiserowitz, M. Lahav and J. Sagiv, Nature 318, 353 (1985).
2. I. Weissbuch, L. Addadi, Z. Berkovitch-Yellin, E. Gati, M. Lahav and L. Leiserowitz, Nature 310, 161 (1984).
3. J.P. Legros and A. Kvick, Acta Cryst. B36, 3052 (1980)
4. (a) R Kern, Bull. Soc. Franc. Mineral. Crist., 76, 391 (1953);
   (b) C.P. Fenimore, A. Thrailkill, J. Am. Chem. Soc., 71, 2714 (1949).
5. C.H. Arrington Jr. and G.D. Patterson, J. Phys. Chem., 57, 247 (1953).
6. M.K. Bernett and W.A. Zisman, J. Phys. Chem., 67, 1534 (1963).
7. (a) M. Seul, P. Eisenberger and H.M.McConnell, Proc. Nat. Acad. Sci. U.S.A., 80, 5795 (1983).
   (b) J. Als-Nielsen and P.S. Pershan, Nucl. Instrum. Meth. 208, 545 (1983);