

Short Communication

Stereochemical studies on chiral systems in two dimensions

Isabelle Weissbuch, Ivan Kuzmenko, Maria Berfeld, Leslie Leiserowitz* and Meir Lahav*

Department of Materials and Interfaces, Weizmann Institute of Science, 76100 Rehovot, Israel

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ABSTRACT: Structural studies on two-dimensional films of chiral amphiphiles at the air–solution interface, as investigated *in situ* primarily by grazing incidence x-ray diffraction (GIXD) using synchrotron radiation, yielded the crystalline packing arrangement at almost the molecular level. Results regarding three different topics are described. (1) It has proven possible to establish whether racemic mixtures of amphiphiles spread on water self-organize into 2-D crystals in which the two enantiomers either form heterochiral domains or spontaneously separate into enantiomorphous islands composed of homochiral molecules. Diastereoisomeric acid–base interactions between two different chiral amphiphiles were also used to achieve spontaneous chiral separation in two dimensions. (2) Ordered binding of solute molecules to the chiral amphiphiles could be applied in order to study their enantioselective interactions with chiral solutes present in the aqueous subphase. (3) Crystalline multilayer films of supramolecular architecture composed of water-soluble and water-insoluble chiral components may be formed at the air–solution interface and their packing arrangement determined by GIXD. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: chiral monolayers; chiral interdigitated multilayers; spontaneous separation of racemic mixtures in 2-D; α -amino acid amphiphiles; mandelic acid amphiphiles; acid–base interactions; diastereoisomeric interactions; grazing incidence x-ray diffraction

INTRODUCTION

The advent of modern surface-sensitive analytical tools has recently revolutionized the field of surface science. In particular, with the availability of intense, monochromatic and coherent x-rays from synchrotron sources, it became possible, by using the method of grazing incidence x-ray diffraction¹ (GIXD), to determine the structure of ordered clusters and thin films, directly on liquid surfaces, almost at the molecular level. Of particular interest is to analyze and monitor structural changes associated with two-dimensional (2-D) chiral systems. Here we summarize recent results from our laboratory with regards to three different topics:

1. Spontaneous separation of racemates in two dimensions.
2. Use of diastereoisomeric interactions in copper complexes of α -amino acids for probing the binding of water-soluble molecules present in the subphase to

polar head-groups of Langmuir films; relevance to crystal nucleation.

3. Formation of multilayer films of diastereomeric two-component amphiphilic molecules with interdigitated hydrocarbon chains.

SPONTANEOUS SEPARATION OF RACEMIC SYSTEMS INTO 2-D ENANTIOMORPHOUS CRYSTALS

Spontaneous separation of enantiomers from a racemic mixture has intrigued scientists since this phenomenon was discovered by Pasteur a century and half ago. Unlike 3-D crystals, the detection of spontaneous separation in 2-D is not straightforward. The method of comparing surface pressure–area isotherms of racemic and chiral Langmuir monolayers² is based on the concept that the shape of the isotherm reflects a phase transformation from a gaseous to a liquid to a homogeneous crystalline monolayer. However, according to GIXD studies, amphiphiles spontaneously form crystalline monolayer islands at very low surface pressures.³ Thus the shape of the surface pressure–area isotherm depends not only on molecular packing within the islands but also upon other factors such as size and shape of the islands and the percentage of non-ordered molecules that lie on island peripheries.

*Correspondence to: M. Lahav or L. Leiserowitz, Department of Materials and Interfaces, Weizmann Institute of Science, 76100 Rehovot, Israel.

E-mail: meir.lahav@weizmann.ac.il

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In principle, the outline of 2-D single crystals delineated by straight boundary lines at the air–liquid interface should reflect the plane group symmetry of the crystal and thus may display chiral hemihedral shapes in the event of enantiomorphous crystals. The latter can be detected by Brewster angle and epifluorescence microscopy.^{4–6} However, imaged 2-D domains were never observed to be single crystals but rather assemblies of crystallites, often assuming dendritic morphologies.^{7–9} Thus optical methods alone do not suffice to establish the presence of spontaneous separation of enantiomers in 2-D crystals.

Experiments involving the detection of chiral segregation in 2-D crystals only began to bear fruit with the use of techniques that probe the structure of thin crystalline films at the nanometer scale. For example, a monolayer, of a tetracyclic alcohol¹⁰ on mica, displaying mirror-image domains was observed by scanning force microscopy (SFM) and the separation of enantiomers of a liquid crystalline biphenyl derivative¹¹ on graphite or that of enantiomorphous clusters of 1-nitronaphthalene decamers on Au(111)¹² were detected by scanning tunneling microscopy (STM). The spontaneous chiral segregation in Langmuir films of a racemic mixture of myristoylanine¹³ has been inferred from GIXD studies.

Molecular packing considerations

The possibility that chiral information may have been transferred across an interface, as an important step in the transformation from a racemic chemistry to chiral biology, prompted us to investigate the separation of a racemic mixture into left- and right-handed 2-D arrays of hydrophobic α -amino acids at the air–water interface.

In order to induce racemic mixtures of amphiphiles to self-assemble, by design, into either homo- or heterochiral monolayer domains on the water surface, it is necessary first to review the fundamental differences in the packing of molecules in three- and two-dimensional crystals. The most common symmetry elements in 3-D crystals are center of inversion, glide plane, twofold-screw axis and translation. In 2-D crystals at a liquid surface, for amphiphile molecules that are specifically oriented *vis-à-vis* the water surface, the situation is simpler. The center of inversion, the glide with its plane parallel to the water surface and the corresponding twofold-screw symmetry are precluded. The only remaining symmetry elements are translation and a glide whose plane is perpendicular to the water surface. Thus, in principle, it should be easier to bring about spontaneous segregation of enantiomeric territories at a liquid surface if the glide symmetry and the possible formation of solid solutions between the two enantiomers are prevented. There is, however, one difficulty in such an approach: the hydrophobic moiety of amphiphilic molecules is generally composed of long aliphatic chains that

tend to pack in the herring-bone motif generated by glide symmetry. Such a molecule may require a functional group within the chain that, together with the hydrophilic group, will promote packing only via translation.

The system of α -amino acid amphiphiles

Reasoning on the above lines was applied to the design of racemic mixtures of α -amino acid amphiphiles, $\text{XHC}(\text{NH}_3^+)\text{CO}_2^-$, to form either of the two hydrogen-bonded monolayer motifs on water surface.¹⁴ In one motif, the molecules are related by glide symmetry as in the racemic crystal structure of norleucine [Fig. 1 (a)]. In the other, the molecules are related by translation as in the α -form of glycine [Fig. 1 (b)]. For the first motif, X was chosen to be a long alkyl chain, $\text{C}_n\text{H}_{2n+1}-$, yielding the amphiphile labeled C_n -gly, to induce the herring-bone motif and thus glide symmetry. In the second motif, X was chosen to be $\text{C}_n\text{H}_{2n+1}\text{CONH}(\text{CH}_2)_4-$, yielding an amphiphile that is a derivative of lysine, labelled C_n -lys, that contains a hydrogen-bonding amide group to promote translation along a 5 Å axis as does glycine itself.

The crystalline structure of monolayers of the two types of amphiphiles on water were elucidated by

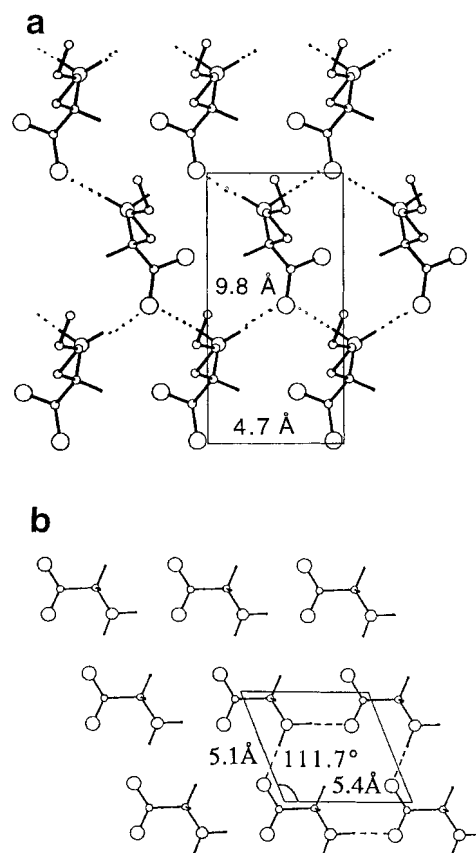


Figure 1. Packing arrangement of the 2-D hydrogen-bonded layers as they appear in the 3-D crystals of (a) (*R,S*)-norleucine and (b) α -glycine

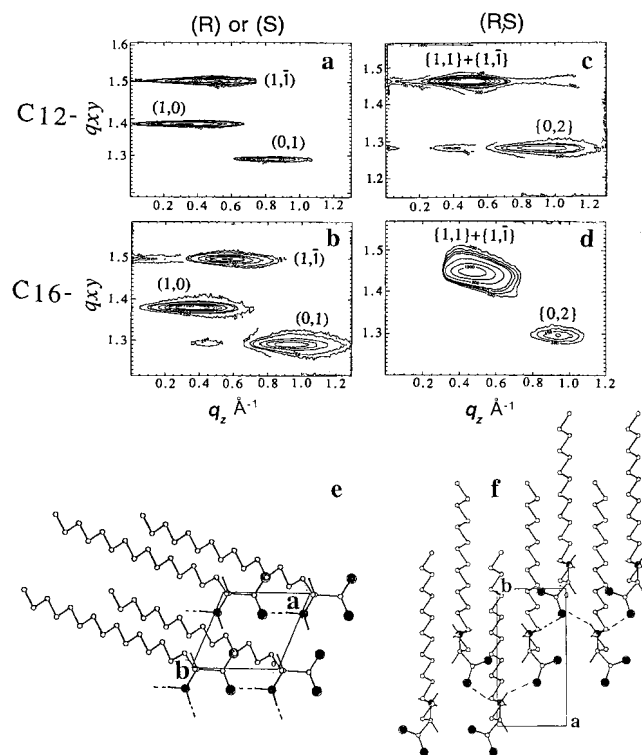


Figure 2. GIXD patterns shown as 2-D intensity contour plots (q_{xy}, q_z) measured from the monolayers of (a) and (b) enantiomerically pure and (c) and (d) racemic C_n -gly, $n = 12, 16$, spread on water; (e) and (f) the corresponding 2-D molecular packing arrangements viewed normal to the water surface

GIXD.¹⁴ The enantiomerically pure (*S*)- C_n -gly, $n = 12, 16$, self-assemble into crystalline domains with molecules related by translation in an oblique unit cell [Fig. 2 (a), (b), (e)]. As anticipated, the molecules of racemic (*R,S*)- C_n -gly, $n = 12, 16$, spontaneously assemble on water into heterochiral crystalline domains containing two molecules related by glide symmetry with herringbone arrangement of the chains in a rectangular unit cell [Fig. 2 (c), (d), (f)]. On the other hand, the crystalline monolayers of C_n -lys, $n = 17, 21$, both in racemic (*R,S*) and in enantiomerically pure (*R* or *S*) form, are essentially iso-structural (Fig. 3), the molecules being related by translation in an oblique unit cell in which the α -amino acid head-groups, $^+H_3NCHCO_2^-$, are interlinked via a 2-D hydrogen-bonded motif as in the 3-D crystal of α -glycine. Thus the introduction of an amide group into the chain induces the racemic mixture to segregate into domains of opposite chirality.

The system of amphiphilic phenylethylamine mandelate salt

Spontaneous separation of enantiomers of two-component monolayer systems¹⁵ has been achieved making use of acid–base interactions in racemic mixtures, by taking

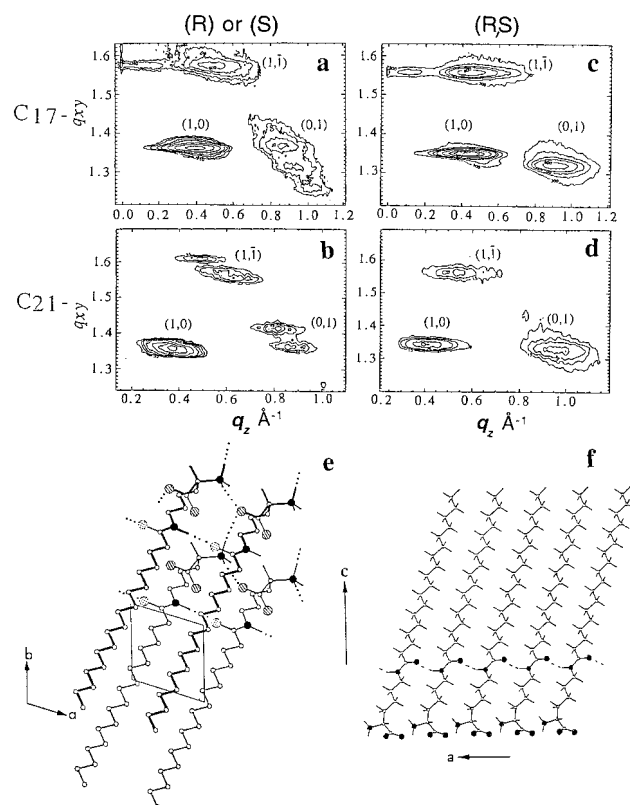


Figure 3. GIXD patterns shown as 2-D intensity contour plots (q_{xy}, q_z) measured from the monolayers of (a) and (b) enantiomerically pure and (c) and (d) racemic C_n -lys, $n = 17, 21$, spread on water; (e) and (f) the corresponding 2-D molecular packing arrangement viewed normal to the water surface and along the *b* axis, respectively

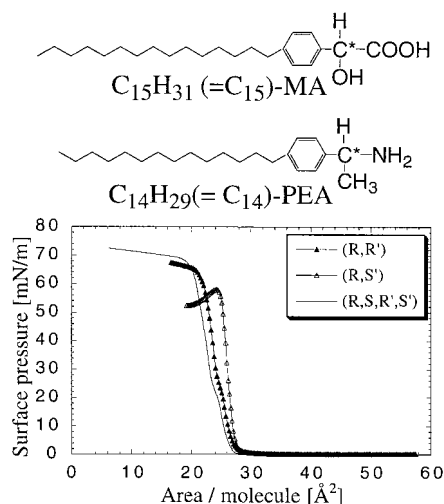


Figure 4. (Top) structural formulas of the C_{15} -MA and C_{14} -PEA molecules; (bottom) surface pressure–molecular-area (π - A) isotherms at 5°C for *R,R'*, *R,S'* and *R,S,R',S'* diastereoisomeric films formed by C_{15} -MA and C_{14} -PEA molecules in a 1:1 molar ratio. The molecular area was calculated per amphiphile molecule, disregarding the difference between them

advantage of the fact that the water-soluble 'homochiral' salt $C_6H_5CH(CH_3)NH_3^+ : C_6H_5CH(OH)COO^-$ is more stable than its diastereoisomeric counterpart.^{16–18} Equimolar mixtures of (*R*)- or (*S*)-*p*-tetradecylphenylethylamine, $C_{14}H_{29}C_6H_4CH(CH_3)NH_2$, and (*R'*)- or (*S'*)-*p*-pentadecylmandelic acid, $C_{15}H_{31}C_6H_4CH(OH)COOH$, form on water stable crystalline monolayers, independent of molecular chirality, as indicated by the similar shape of the π -*A* isotherms (Fig. 4).¹⁹

The GIXD patterns measured from the *R,R'* and *R,S'* mixtures are clearly different both in terms of positions of the Bragg peaks, their integrated intensities [Fig. 5 (a), (c), left] and, in particular, the shapes of the corresponding Bragg rods [Fig. 5 (d)], whereas the mixture *R,S,R',S'* [Fig. 5 (b), left] displays a diffraction pattern almost identical with that of the *R,R'* monolayer. Since the oblique unit cell derived for *R,S,R',S'* contains only two independent molecules and the monolayer is highly crystalline in view of the narrow Bragg peaks, it is highly plausible that the *R,S,R',S'* mixture segregates into *R,R'*

and *S,S'* crystalline islands of opposite handedness. The crystallization process for the three systems is shown schematically in Fig. 5 ((a)–(c), right).¹⁹

More detailed studies, however, demonstrated that a substantial degree of mixing of the enantiomers takes place within these phases. The possibility of chiral disorder for the MA moiety may be drawn from the reported 3-D structure of (*R*)-MA:(*S*)-*C*₁-PEA with an intra-layer cell that compares well with those of the diastereoisomeric monolayers. The interchange of the OH group with the hydrogen atom at the chiral carbon center with the concomitant switch in chirality of MA leads to the formation of an additional hydrogen bond while not impairing van der Waals contacts. Experimental proof for such a type of chiral disorder was provided by the observation of a similar disorder between the enantiomers in the 3-D crystal structure of the salt (0.45*R*,0.55*S*)-*C*₁₅-MA:(*R*)-PEA, where the structure refinement revealed about 50% chiral disorder of the OH group of the acid component.¹⁹

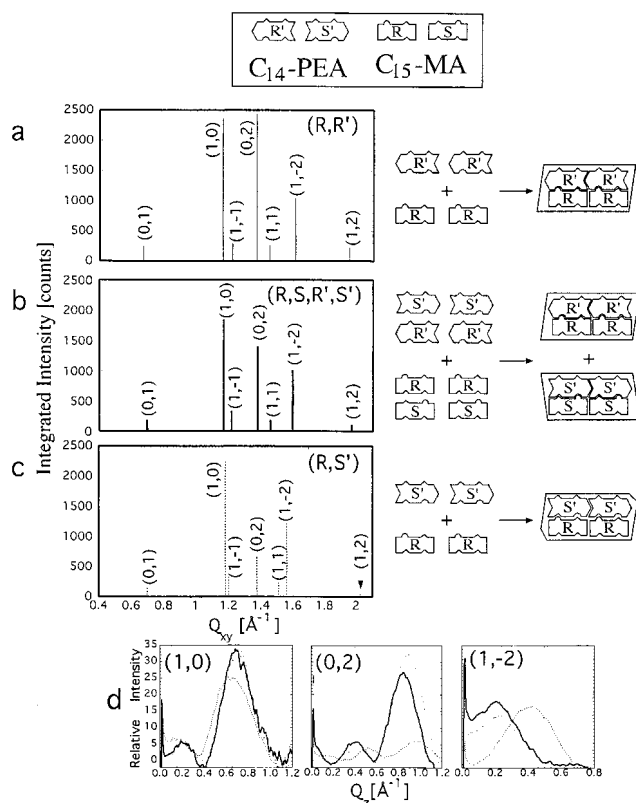


Figure 5. GIXD patterns for the three diastereoisomeric films, *R,R'* (thin line), *R,S'* (dotted line) and *R,S,R',S'* (thick line), measured at 5 °C and surface pressure $\pi = 1 \text{ mN m}^{-1}$. (a)–(c), left: the observed Bragg peaks are represented by lines of the corresponding integrated intensities with assigned (*h*,*k*) indices. (d) Comparison of Bragg rods of the three diastereoisomeric systems corresponding to the most intense (1,0), (0,2) and (1,-2) reflections, where line style corresponds to that as in (a)–(c), left; (a)–(c), right. Schematic views of the molecular assembly into crystals corresponding to the three diffraction patterns

LANGMUIR FILMS OF DIASTEREOMERIC COPPER COMPLEXES OF α -AMINO ACIDS AT THE AIR–SOLUTION INTERFACE

Clusters formed in supersaturated solutions have been shown to play a ubiquitous role in crystallization processes. We proposed that among structured clusters there are those that resemble the structure of the macroscopic, 3-D crystalline phase. Based on this hypothesis, it became possible to design auxiliary molecules that can be stereospecifically and enantioselectively targeted at the surfaces of undesired clusters and inhibit their growth.²⁰ This methodology was successfully applied for the control of crystal polymorphism,^{21–23} inducing^{24,25} and preventing²⁶ crystal twinning and the optical resolution of enantiomers by kinetic crystallization.^{27,28} Several decades ago, the crystallization of copper complexes of racemic aspartic acid in the presence of optically pure α -amino acids, e.g. (*S*)-glutamic acid, was reported by Harada²⁹ to result in the precipitation of the (*R,R*)-aspartate–copper complex. To explain this induction process, one can propose that the copper complex of (*S*)-glutamic acid interacts enantioselectively and inhibits the growth of the (*S*)-aspartate clusters thus preventing their conversion to the 3-D crystals.³⁰ This mechanism appears to be of general applicability as demonstrated for a large number of systems.³¹

One way to obtain information on interactions between clusters and chiral molecules is by studies on the oriented growth of crystals at the air–solution interface induced by enantiomerically pure long-chain amphiphile molecules. For example, crystals of the centrosymmetric α -form of glycine were found to be attached beneath the monolayer via one of the two enantiotopic (010) or (0 $\bar{1}$ 0) faces,

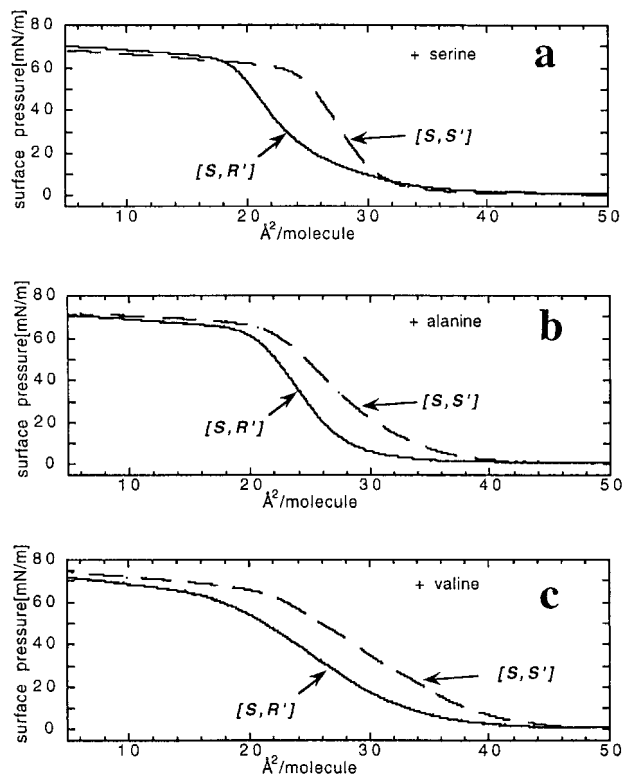
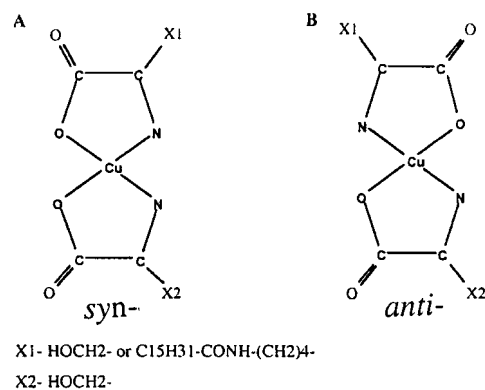


Figure 6. Surface pressure–area isotherms showing the effect of injection of (a) serine, (b) alanine and (c) valine into the copper acetate aqueous subphase beneath the monolayer. S,S , S,R refer to the absolute configuration of the S amphiphile spread on the subphase to which S or R water-soluble α -amino acids were injected

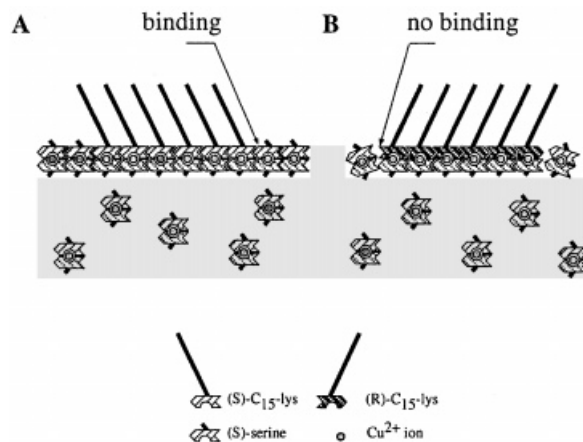
depending on the absolute configuration of the monolayer molecules.³² Such observations led to the conclusion that the water-insoluble, long-chain, α -amino acid amphiphiles, at the air–solution interface, spontaneously form crystalline domains whose polar head-groups serve as template for an epitaxial nucleation of 3-D α -glycine crystals.¹⁴

Reasoning on the above conclusions, the diastereoisomeric interactions between long-chain copper– α -amino acid complexes, at the air–solution interface, and water-soluble α -amino acid complexes present in the aqueous subphase were investigated.³³ The Cu^{2+} ions bind both to an α -amino acid head-group of the insoluble amphiphile and to the water-soluble α -amino acid molecules from the aqueous subphase. Langmuir films of enantiomerically pure (S)- or (R)- and racemic (R,S)- N^{ϵ} -palmitoyllysine and α -aminostearic were investigated on copper acetate solutions without and in the presence of enantiomerically pure (S)- or (R)-alanine, -serine and -valine [hereafter labeled R or S]. The surface pressure–area (π - A) isotherms showing the effect of the water-soluble serine, alanine or valine addition to the copper acetate aqueous solution beneath the monolayer of the (S)- N^{ϵ} -palmitoyllysine are shown in Fig. 6. The π - A isotherms for the systems of the same absolute configuration, say amphi-



Scheme 1

phile S and solute S , are always more expanded as compared to those of the diastereoisomeric molecules S and R . These diastereoisomers assume different packing arrangements, as demonstrated by GIXD measurements of the films directly at the air–solution interface.³³ Furthermore, on the basis of comparative x-ray photoelectron spectroscopic (XPS) studies of the films of the two types of hetero-complexes and 3-D crystals of (S)-serine and (R,S)-serine Cu complexes, the configuration of the α -amino acid ligands around the Cu^{2+} ions in these complexes indicated a structural similarity. In the thin films the S -Cu- S complex displays a *syn* configuration whereas the S -Cu- R complex adopts an *anti* configuration (Scheme 1). We rationalized the observed more expanded π - A isotherms of the amphiphile and solute of the same absolute configuration by proposing that water-soluble S -Cu- S complex molecules of *syn* configuration can bind stronger to the periphery of the polar head-groups of the monolayer islands of S -Cu- S of the same absolute configuration by virtue of a better molecular fit. Because of steric hindrance, the S -Cu- S complex molecules may bind only loosely to the periphery of the S -Cu- R domains that assume an *anti* configuration (Scheme 2). This preferred and stereoselective attach-



Scheme 2

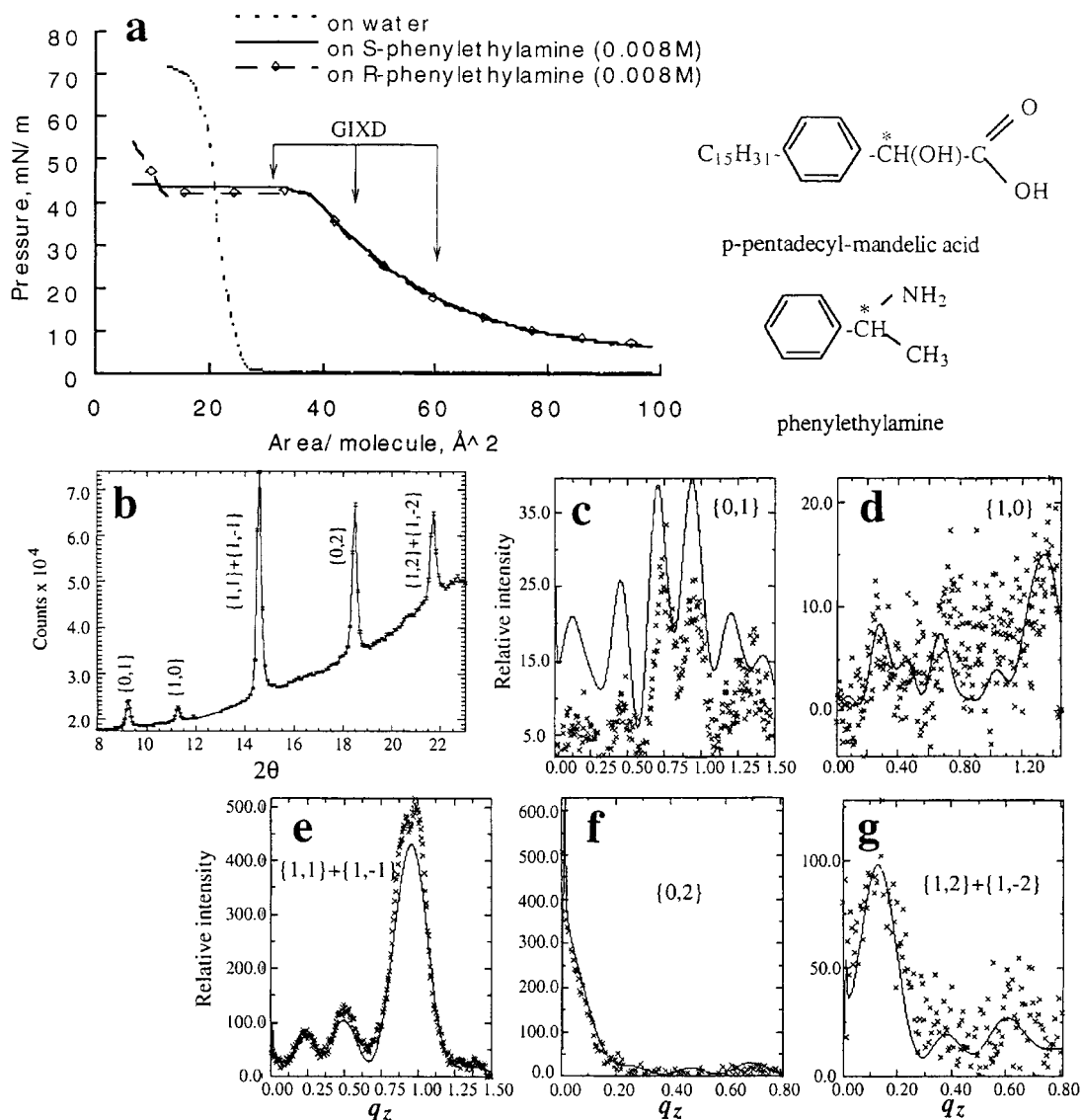


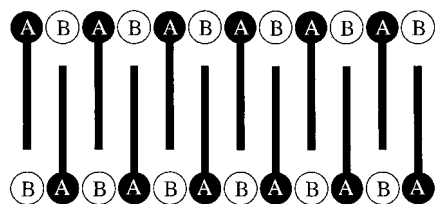
Figure 7. (a) Surface pressure–molecular area (π -A) isotherms of (*R*)-C₁₅-MA on Millipore water and on PEA aqueous solutions. The arrows show the states at which GIXD patterns were recorded and SFM measurements for the corresponding LB films were performed. (b)–(g) GIXD patterns of (*R*)-C₁₅-MA spread on (*R*)-PEA and compressed to 30 Å² per molecule at 5°C: (b) the observed GIXD Bragg peaks with assigned (h,k) indices, where 2θ corresponds to the in-plane component of the scattering vector q (wavelength $\lambda = 1.339$ Å); (c)–(g) the corresponding measured (crosses) and calculated (solid line) Bragg rod intensity profiles, $I(q_z)$ based on a molecular model

ment leads to a larger effective domain size of the *S*-Cu-*S* complex and thus to a more expanded isotherm. Consequently, the energy required for the removal of the attached molecules by compression is larger for the complex of the same absolute configuration than those of opposite configuration.

FORMATION OF MULTILAYER FILMS OF DIASTEREOISOMERIC TWO-COMPONENT AMPHIPHILIC MOLECULES WITH INTERDIGITATED HYDROCARBON CHAINS

A way to construct stable supramolecular architectures at

the air–water interface is by spreading a water-insoluble, long-chain acid on an aqueous solution containing a complementary amine.¹⁵ Compression of the film causes alternating acid–base groups to emerge at either side of the membrane whereas the central part contains the interdigitated hydrophobic groups of the acid in space-filling contact across a central plane (Scheme 3). Both acidic (A) and basic (B) head-groups are attached to a chiral carbon center, and the layering and ordering in these films differ greatly between diastereoisomeric salts of *R,R* and *R,S* absolute configuration. In a search for appropriate bimolecular systems that satisfy the above criteria, we made use of the diastereoisomeric phenylethylamine mandelate salts. The 3-D crystal structure of



Scheme 3

the 1:1 salt of phenylethylamine (PEA) and mandelic acid (MA) molecules, both of the same absolute configuration, is characterized by rigid hydrogen-bonded bilayers. The phenyl rings are positioned and oriented in a way that is compatible with the formation of an interdigitated arrangement when either the acid or the amine would be modified by attaching a long hydrocarbon chain in the *para*-position of its phenyl group. The 3-D crystal structure of phenylethylamine mandelate salt composed of molecules of opposite handedness, say (*R*)-MA and (*S*)-PEA, also contain hydrogen-bonded bilayers, but their phenyl rings are not aligned in a way suitable for the formation of an interdigitated packing motif.^{16–18} The surface pressure–area isotherms of (*R*)-*p*-pentadecylmandelic acid spread on aqueous solutions containing (*R*)- and (*S*)-PEA have similar shapes [Fig. 7 (a)]. Both isotherms are expanded and reach a plateau at an area $A \approx 40 \text{ \AA}^2$ and $\pi = 42 \text{ mN m}^{-1}$. The GIXD measurements [Fig. 7 (b)–(g)] were performed on the two types of films at different points along the isotherm, as indicated by arrows in Fig. 7 (a).

The film of (*R*)- $C_{15}H_{31}$ -MA over an aqueous solution of (*S*)-PEA did not diffract at any point along the isotherm. In contrast, replacement of the aqueous solution by (*R*)-PEA gave rise to a strong GIXD pattern after compression to $A \approx 30 \text{ \AA}^2$ [Fig. 7 (b)–(g)]. The film structure (Fig. 8), determined to near atomic resolution, is an interdigitated crystalline trilayer whose alkyl chains

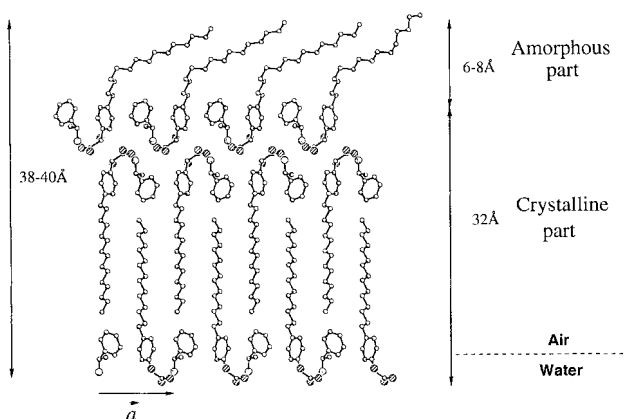


Figure 8. Packing arrangement of the interdigitated, (*R*)- C_{15} -MA:(*R*)-PEA, trilayer viewed along the *b* axis. Amorphous and crystalline parts are indicated by the upper and lower arrows at the right

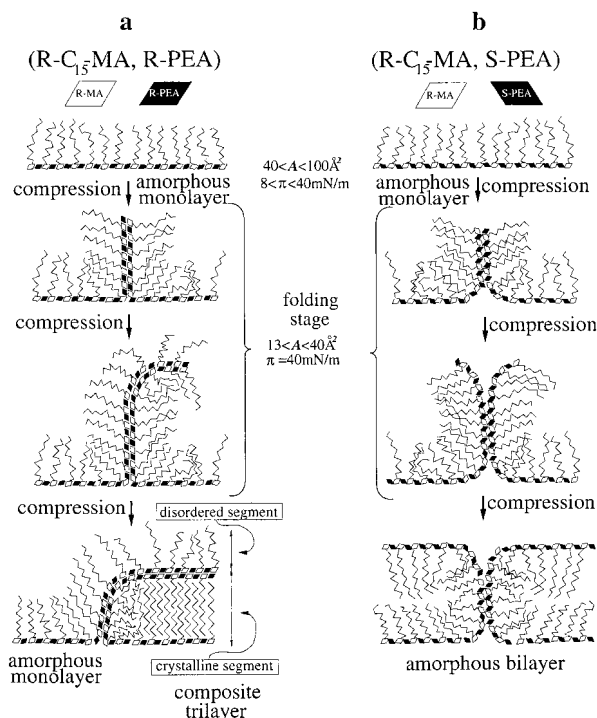


Figure 9. Schematic representation of a simple mechanism for the formation of a crystalline trilayer of the *R,R* diastereoisomer

exposed to air are disordered because of the gaps created by the interleaved PEA units. The absence of an ordered interdigitated structure for the (*R*)- $C_{15}H_{31}$ -MA:(*S*)-PEA system was interpreted in terms of the incompatibility between the packing of the chains and the head-groups. A model for the process of molecular reorganization as a function of film compression for the (*R*)- $C_{15}H_{31}$ -MA:(*R*)-PEA system is depicted in Fig. 9. Complementary information on the thickness of the *R,R* and *R,S* films, after transfer from the air–solution interface on to a freshly cleaved mica support, was obtained by SFM studies (Fig. 10). The SFM images suggested the formation of an interdigitated molecular arrangement for the *R,R* film, whereas the *R,S* film appeared to form a non-crystalline bilayer. In an analogous manner, crystalline interdigitated films were formed from a variety of other types of binary acid–base systems. It appears that the basic requirement for chains interdigitation is the spontaneous formation of an initial mixed monolayer comprising the complementary acid–base components in proper registry, despite the loss in effective chain packing. In the next step, the system will pack into a crystalline architecture only if the chains are interdigitated. The presence of interdigitation for other systems, including amphiphilic acids with short-chain benzamidiinium bases, has been demonstrated more recently in studies performed also with the relevance to the origin of self-replicating systems (in collaboration with Dr M. Kindermann and Professor G. von Kiedrowski).

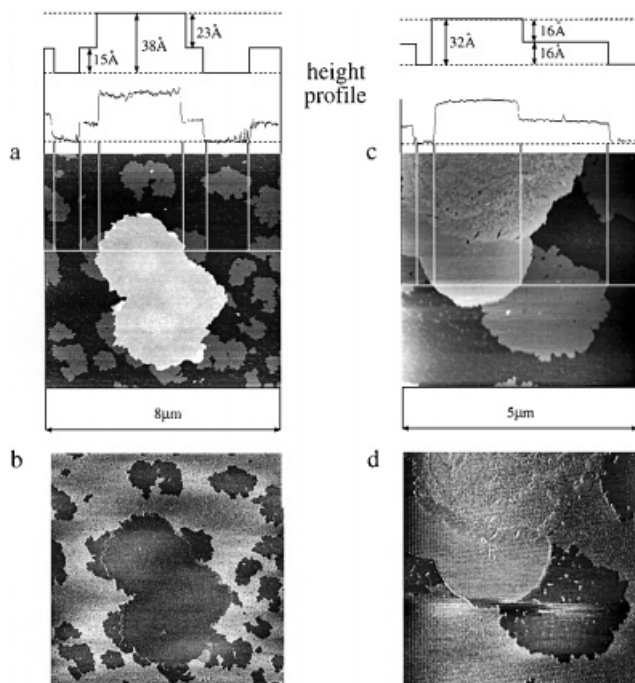


Figure 10. SFM images and the corresponding height profiles of films transferred on to freshly cleaved mica by the LB technique: (a), (b) (*R*)-C₁₅-M:(*R*) PEA and (c), (d) (*R*)-C₁₅-MA:(*S*)-PEA. (a), (c) represent topography and (b), (d) friction-force images

OUTLOOK

We have reviewed some of our structural studies on 2-D crystalline films of amphiphilic molecules at the air-solution interface. The self-organization of such molecules was investigated *in situ* primarily by GIXD using synchrotron radiation, and the molecular packing arrangements of the crystalline films were determined.

It has proven possible to establish whether racemic mixtures of amphiphiles spread on water self-organize into 2-D crystals in which the two enantiomers either form heterochiral domains or spontaneously separate into enantiomorphous islands composed of homochiral molecules. Diastereoisomeric acid-base interactions between two different chiral molecules were also used to achieve spontaneous chiral separation at the air-water interface.

Ordered binding of solute molecules to the chiral amphiphiles could be applied in order to study their enantioselective interactions with chiral solutes present in the aqueous subphase. Crystalline multilayer films of supramolecular architecture composed of water-soluble and water-insoluble chiral components may be formed at the air-solution interface and their packing arrangement determined by GIXD.

The GIXD technique is not confined to amphiphilic molecules alone but may be applied to a variety of hydrophobic water-soluble and water-insoluble molecules, thus opening new ways to investigate molecular self-organization in two dimensions for systems of higher

degree of complexity followed by subsequent dynamic processes. Such systems may be of relevance to a better understanding of the early stages of 3-D crystal nucleation and polymorphism control. Studies along these lines are under investigation.³⁴

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