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Effect of chirality on monoacylglycerol ester monolayer characteristics: 3-Monopalmitoyl-*sn*-glycerol

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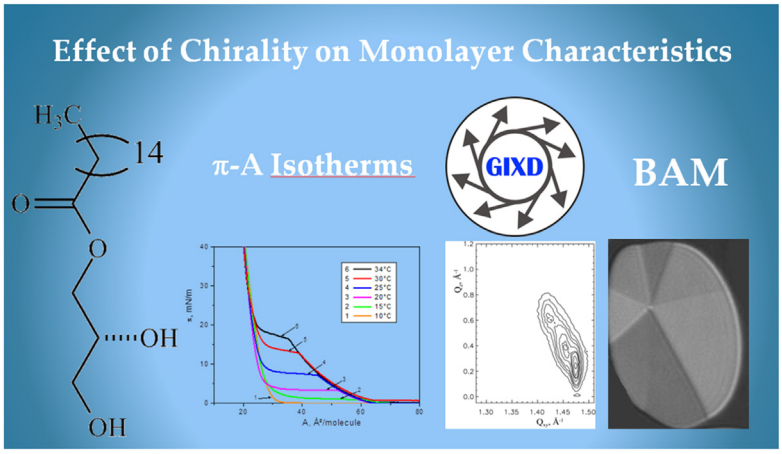
HIGHLIGHTS

- The influence of chirality on the thermodynamic behavior, the morphological features, and the 2D lattice structures is characterized.
- Preferred heterochiral interaction is indicated by comparison of the transition entropy of the enantiomeric and racemic forms.
- The dominance of the chiral nature is indicated by the contour plots displaying three separated diffraction signals.
- The small effect of chirality on the lattice structures is demonstrated by the similarity of the lattice data obtained by fitting 3 and 2 peaks.
- The influence of chirality on the lattice distortion is weak and decreases with increasing temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of chirality on the thermodynamic behavior, the morphological features, and the 2D lattice structures of 3-monopalmitoyl-*sn*-glycerol monolayers is studied. The results are based on measurements of the surface pressure-area (π-*A*) isotherms, Brewster angle microscopy (BAM), and Synchrotron X-ray diffraction at grazing incidence (GIXD). The π-*A* isotherms of the enantiomeric 3-monopalmitoyl-*sn*-glycerol monolayers measured between 10 and 34 °C are similar to those of the racemic 1-monopalmitoyl-rac-glycerol monolayers. Evaluating the temperature dependence of the phase transition pressure (π_t) gives access to the transition entropy. The absolute ΔS values increase as the temperature decreases demonstrating that the ordering of the condensed phase increases at lower temperatures. The comparison with the corresponding racemate shows that the condensed phase of the racemate has a higher stability indicating preferred heterochiral interactions. Similar to the racemic monoglycerol esters round and cardioid-like domains are observable but the tendency to irregular deviations in the inner texture and shape from the perfect circular domain in the mesoscopic domain topography is larger for the chiral 3-monopalmitoyl-*sn*-glycerol than for the racemic 1-monopalmitoyl-rac-glycerol. Systematic GIXD measurements of 3-monopalmitoyl-*sn*-glycerol monolayers are carried out over large pressure intervals at 5, 10, and 15 °C. The comparison of the contour plots for the three temperatures shows a shift of the contour plots displaying three separated diffraction signals, which indicate the dominance of the chiral nature, to higher lateral pressures with increasing temperature. The similarity of the lattice data obtained by fitting 3 and 2 peaks for conditions where the contour plots resemble those of NN tilted or NNN tilted orthorhombic structures demonstrates the

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small effect of chirality on the lattice structures in this region.
The cross-sectional area, A_0, is almost unaffected by surface pressure and temperature and amounts to values between 19.7 Å^2 and 19.8 Å^2, as expected for a rotator phase at the lower limit. The tilt angle with respect to the surface normal t decreases with increasing pressure. The tilting transition pressure was obtained by plotting $1/\cos(t)$ vs. the lateral pressure and extrapolating to the zero tilt angle. The values for the untilted state are quite high and have not been reached experimentally, but they are slightly smaller than those of the corresponding racemic mixture. The lattice distortion d plotted versus $\sin^2(t)$ and extrapolated to zero tilt provides the d_0 values which are slightly smaller than 0 showing that the influence of chirality on the lattice distortion is weak and decreases with increasing temperature.

1. Introduction

Chirality-based phenomena are of permanent interest. In particular, design and characterization of molecules which can form hierarchical chiral nanoarchitectures is in the focus of the current attention [1]. Amphiphiles represent one of the important building blocks which can develop chiral nanoarchitectures. Studies of chirality in amphiphilic monolayer systems seem promising to serve as model systems [2]. The purpose of such studies has been primarily to understand chirality-dependent interactions in monolayers [3,4].

Monoacylglycerols are naturally occurring amphiphiles existing in a large diversity of biological systems [5,6]. They have a glycerol backbone linked by an ester group to an alkyl chain. The aliphatic chain positioned at one end of the glycerol backbone gives rise to an optically active carbon atom in C-2 position. Palmitoyl- and stearoyl-glycerol have been the most examined saturated monoacylglycerol monolayers because of their omnipresence in biological and applied systems [7–9]. Langmuir monolayers can be used as simple model systems for understanding the role of monoacylglycerols in inherently complex biological processes and solid lipid nanoparticles for drug delivery systems.

Monoacylglycerols are interesting amphiphiles that make the comparison of the enantiomeric and racemic monolayers possible. Chiral discrimination effects have been already found for monoacylglycerol ethers [10–12], esters [13–17], amines [18,19] and amides [20] using BAM, fluorescence microscopy and GIXD.

In recent papers [21,22], the racemic 1-monopalmitoyl-*rac*-glycerol and 1-monostearoyl-rac-glycerol monolayers were comprehensively characterized in mesoscopic and molecular scales using Brewster angle microscopy (BAM) and Grazing incidence X-ray diffraction (GIXD). Using 1-monopalmitoyl-*rac*-glycerol monolayers mesoscopic domains with perfect topography were found that allowed the geometric analysis of the inner segment structure. The segment boundaries of the 1-monopalmitoyl-*rac*-glycerol monolayer domains were interpreted as dense lattice rows. Similar mesoscopic domain topography was found for the domains of the homologous 1-monostearoyl-*rac*-glycerol.

Systematic GIXD measurements of monolayers of 1-monostearoyl-*rac*-glycerol and 1-monopalmitoyl-*rac*-glycerol were carried out in the accessible ranges of temperature and surface pressure to construct a phase diagram on the basis of reliable 2D lattice structures. First evidence for symmetry breaking in a monolayer of a racemic surfactant was obtained by the finding of an oblique intermediate phase between the NN and NNN tilted orthorhombic phases in the racemic 1-monostearoyl-*rac*-glycerol monolayer at low temperatures in a small pressure region. The surface pressure–temperature (π-T) phase diagram of 1-monopalmitoyl-*rac*-glycerol monolayers provides additional information about the effect of alkyl chain length and temperature on the phase behavior in more detail. At the low temperatures of 5 and 10 °C, a direct first-order phase transition between the NN and NNN tilted orthorhombic phases connected with a jump in the tilt direction takes place, whereas at T ≥ 15 °C only the NN-tilted orthorhombic lattice structures exist. A generalized phase diagram for racemic long chain 1-monoacylglycerols has been constructed on the basis of the comparison of the π-T phase diagrams of the homologous 1-monopalmitoyl-*rac*-glycerol and 1-monostearoyl-*rac*-glycerol. These general insights into the monolayer characteristics of the racemic monoacylglycerols represent a good prerequisite to obtain information on the effect of chirality-dependent interactions in the chiral acylglycerol monolayers. The present work focuses on the main characteristics of 3-monopalmitoyl-*sn*-glycerol.

2. Experimental

3-Monopalmitoyl-*sn*-glycerol (Sigma, purity ≥99 mol%) was dissolved in heptane/ethanol (9:1) (Merck p.a. grade). Ultrapure water with a specific resistance of 18.2 MΩ cm, obtained from a Millipore desktop system, was used for the monolayer experiments.

The equilibrium surface pressure-molecular area (π-A) isotherms, recorded at a compression rate of ≤10 Å^2/(molecule·min), were measured with an experimental setup consisting of a self-made, computer-interfaced film balance [23] using the Wilhelmy method with a roughened glass plate to measure the surface tension with an accuracy of ±0.1 mN/m. The accuracy of the molecular area was ±0.5 Å^2. BAM measurements were carried out using the Nanofilm-UltraBAM, Accurion GmbH, Göttingen. Detailed information about the BAM method is given elsewhere (see, e.g., refs 19–21 and references therein). The grazing incidence X-ray diffraction (GIXD) measurements were performed at the BW1 beamline, HASYLAB (Hamburg, Germany).

The thermostated Langmuir film balance was placed in a hermetically closed container filled with helium. A monochromatic X-ray beam (λ = 1.304 Å) strikes the water surface at a grazing incidence angle $\alpha_i = 0.85\ \alpha_c$ (where $\alpha_c = 0.13°$ is the critical angle for total reflection of the X-ray beam at the water surface) illuminating approximately 2 × 50 mm^2 monolayer surface. The trough is slowly laterally moved during the experiment, to avoid sample damage by the strong X-ray beam.

A linear position-sensitive detector (PSD, OEM-100-M, Braun, Garching, Germany) measured the diffracted signal and was rotated to scan the in-plane Q_{xy} component values of the scattering vector. The vertical channels of the PSD measured the out-of-plane Q_z component of the scattering vector between 0 and 0.85 Å^{-1}.

The analysis of the obtained diffraction patterns provides information about the lattice structure of the monolayer. The Bragg peaks, obtained by integration of the scattering intensity (corrected for polarization, effective area, and Lorentz factor) over a certain Q_z window, and the Bragg rods, obtained by the integration of the scattering intensity over a certain Q_{xy} window, give the data about the unit cell dimensions (lattice parameters a, b, c, in-plane area A_{xy}, cross-sectional area A_0, tilt angle t). The

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