Chiral Discrimination and Phase Features of Long-Chain Monoglycerolester Monolayers at the Air/Water Interface

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Amphiphilic monolayers with one or more chiral centers represent unique systems to study chirality-dependent interactions under defined conditions. In recent years, first information has been obtained about the influence of chirality on the phase properties of monoglycerol ester monolayers. However chiral discrimination in the phase behaviour and lattice structure was found only for stearoylglycerol monolayers at 5 °C whereas at 20 °C and for mono-palmitoylglycerol no effect of the chiral centre has been observed. A systematic comparison of the phase and lattice features of the racemic and enantiomeric forms of monoglycerolesters at different temperatures can help to understand in more detail the reason for the differences presented in our previous work [1]. Here, the results of 1-stearoyl-*rac*- glycerol (R-Gl)and 3-stearoyl-*s,n*-glycerol (E-Gl) are presented.

Basically, the same three types of contour plots were found in monolayers both of R-Gl and E-Gl. indicating that three types of condensed monolayer phases occur in both chiral forms.. A centred rectangular lattice with a chain tilt in NN direction is indicated by two in-plane diffraction peaks at $Q_z = 0$ Å^{-1} and at $Q_z > 0$ Å^{-1}. Usually, it occurs in the lowest pressure range. Also a centred rectangular lattice but with chain tilt in NNN direction occurs at higher surface pressures and is indicated again by two reflexes, both located at $Q_z > 0$ Å^{-1}.

An additional phase with an oblique chain lattice and a chain tilt in an intermediate (I) direction appears very frequently between the NN and NNN phases. The NN $\rightarrow$ NNN phase transition splits in two successive NN $\rightarrow$ I and I $\rightarrow$ NNN transitions. Whereas the NN $\rightarrow$ I transition occurs abruptly, the I $\rightarrow$ NNN transition takes place continuously.

The surface pressure – temperature diagrams demonstrate that all three phases occur both in the enantiomeric (R-Gl) (Figure 2) and in the racemic (R-Gl) monolayers (Figure 3) though the phase transition pressures are completely different for enantiomeric and racemic form. Consequently, the chiral discrimination effect cannot be overseen. In both cases, the NN $\rightarrow$ I transition changes linearly to higher pressures with increasing temperature. It is at zero pressure at 5 °C but the slope of the straight line is stronger for R-Gl. The portion of the I-phase is very different for both substances. In the racemic R-Gl monolayer the I-phase exists only at low temperatures in a small pressure region (see Figure 3)so that it was overseen in previous work. At 20 °C already, the I phase disappears and a direct NN $\rightarrow$ NNN transition takes place. On the other hand, in the enantiomeric E-Gl monolayers the I-phase exists over a broad pressure range at all temperatures but at low temperatures it is so dominant that at 5 °C it was found over the whole accessible pressure range. Particularly in the E-Gl monolayers the I $\rightarrow$ NNN transition is so continuous that it cannot exactly determined but at T $\geq$ 10 °C the NNN phase exists at high surface pressures. In the racemic R-Gl monolayer the NNN phase dominates over a large pressure range increasingly with decreasing temperatures.

First studies of the corresponding racemic and enantiomeric palmitoylglycerol monolayers suggest that the data do not follow a simple shift according to a generalised phase diagram.

[1] U. Gehlert, D. Vollhardt, G. Brezesinski, H. Möhwald, Langmuir 12, 4892 (1996).

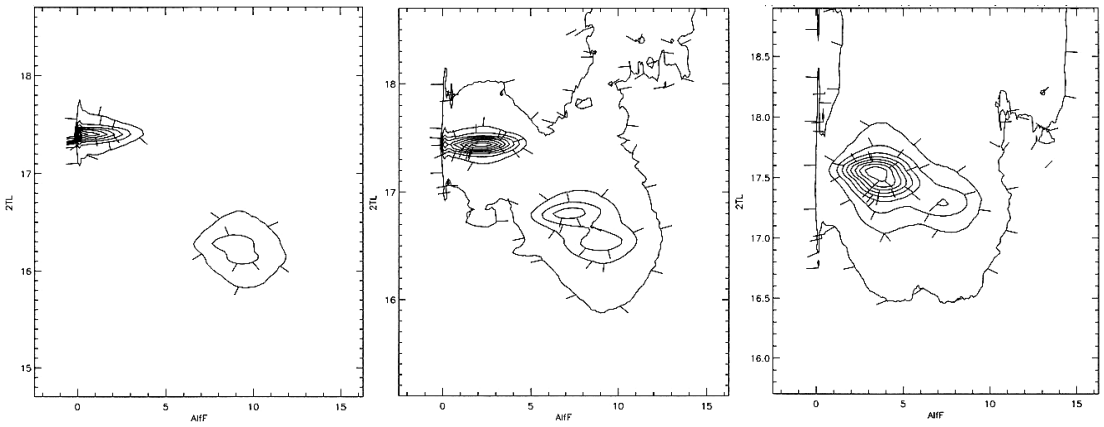

Figure 1: 3 characteristic contour plots of the diffracted intensity vs the in-plane scattering angle (2θ) and the out-of-plane scattering angle (α_f) for the enantiomeric 3-monostearoyl-sn-glycerol monolayer; π = 10 (NN phase), 20 (I phase), 40 mN/m (NNN phase) from left to right; T = 15 °C

Figure 2: Surface pressure –temperature diagram of the enantiomeric 3-stearoyl-*s*,*n*-glycerol monolayer

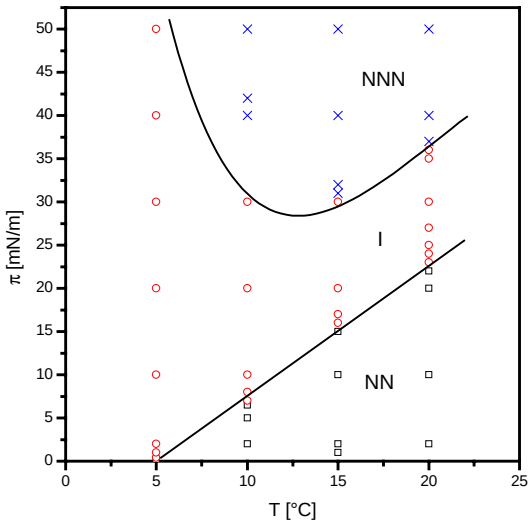

Figure 3: Surface pressure –temperature diagram of the racemic 1-stearoyl-*rac*-glycerol monolayer