

Cross-sectional area increase at phase transition on compression: A new unexpected phenomenon observed in an amide monolayer

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The characteristic features of Langmuir monolayers are sensitively determined by the chemical structure of the amphiphiles. In recent years, interesting information has been obtained on the effect of small changes in the molecular structure of the amphiphile on the main characteristics of the monolayer, in particular the surface pressure –area per molecule (π - A) isotherms, the shape and texture of the condensed phase domains, and the two-dimensional lattice structure [1]. Monolayer studies of model amphiphiles containing amide and amine groups attracted attention because these groups are integral part of the general structure of sphingolipids, which seem to play an important role in those membrane parts that allow the transport into the cells, and of naturally occurring N-acylethanolamines and their precursors, N-acylphosphatidylethanolamines with respect to their metabolism and their interaction with other membrane lipids and proteins.

Studies of 3-hydroxy-N-tridecyl propanoic acid amide ($C_{13}H_{27}-NH-CO-C_2H_4OH$, HTPA) monolayers have shown a phase transition between two condensed phases which is accompanied by an abrupt change of important 2D lattice parameters, such as molecular tilt angle and unit cell area A_{xy} , obtained by grazing incidence X-ray diffraction (GIXD). Despite the drastic changes in the lattice parameters both condensed phases had an oblique lattice. These unusual properties were the reason to perform further careful studies of the phase behavior and lattice structure of HTPA monolayers. Thorough GIXD studies have revealed a new phenomenon, to the best of our knowledge never observed before. The cross sectional area (A_0) of the alkyl chain of HTPA jumps from a smaller value in the phase at lower surface pressure to a larger value in the phase existing at higher pressure [2]. The opposite behavior should be expected and is usually noted in the lattice structures of Langmuir monolayers. The present work focuses on this new interesting phenomenon.

Figure 1, left, shows two π -A isotherms of the HTPA monolayers as characteristic example for the low temperature range at 3 °C and for the high temperature range at 15 °C. Both isotherms show a sharp inflection point followed by an inclined plateau indicating the first-order fluid/condensed phase transition. The lateral pressure of this main transition increases linearly with increasing temperature with a slope of 1.405 mN/m·K⁻¹. It is interesting to note that, at low temperatures, the π -A isotherms reveal a striking second weak inflection point at $A < A_c$, indicating the existence of a second phase transition between two condensed phases. The area change after the second inflection point is very small compared with the main phase transition. The transition pressure of this second phase transition is nearly independent of temperature and amounts to ~17.5 mN/m. Therefore, the transition cannot be seen anymore at ≥10°C because then the main transition pressure is already higher than the expected pressure of this second phase transition. The formation of the condensed phase within the fluid/condensed phase transition region has been visualized by BAM experiments (Figure 1, right). At the beginning of the inclined plateau of the isotherms, domains with six straight main axes grow from a small round centre in a regular distance of about 60 degrees from each other independent of the temperature.

The crystalline domains in the monolayer at the air/water interface were investigated using grazing incidence X-ray diffraction measurements at the BW1 beamline, HASYLAB (DESY, Hamburg, Germany). Figure 2, left, shows selected contour plots of the corrected X-ray diffraction intensities as a function of the in-plane scattering vector component Q_{xy} and the out-of-plane scattering vector component Q_z obtained at different lateral pressures and temperatures. The three Bragg peaks observed at all pressures and the two temperatures (3 and 15°C) investigated show that the structure of the monolayer remains oblique up to high lateral pressures. The alkyl chains are strongly tilted in a non-symmetry direction. At 3°C, the observed structure at lateral pressures below the transition between the two condensed phases is quite similar to that of a rectangular unit cell with

NN-tilted alkyl chains. At the transition pressures of ~ 17.5 mN/m, the structure changes to a more oblique lattice. As seen in Figure 3, similar contour plots, but with different peak and rod positions, have been found at higher temperature (15°C). This means that the phase observed above the fluid/condensed (LE/LC) transition at higher temperature has a similar structure as that observed at high pressure and low temperatures.

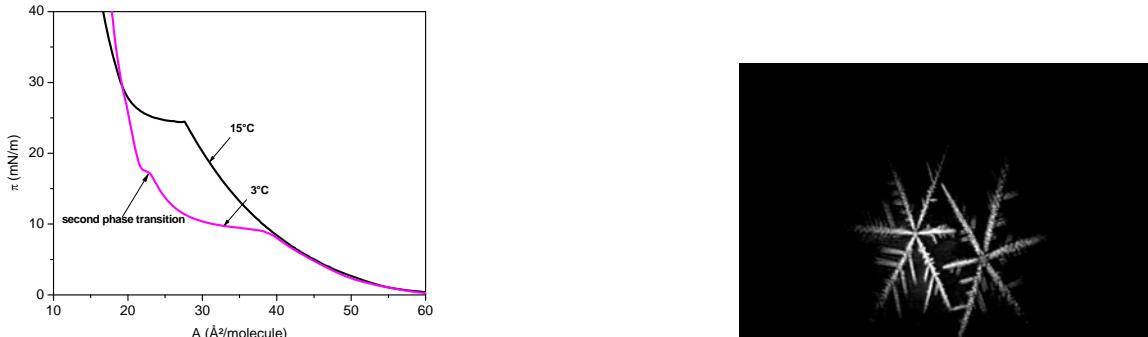


Figure 1: Left) π - A isotherms of HTPA monolayers spread on water at 3°C and 15°C . Right) Domains within the fluid/condensed transition region of the isotherms of HTPA.

The cross sectional area (A_0) of the alkyl chain of HTPA jumps from a smaller value in the phase at the lower surface pressure to a larger value in the phase existing at higher pressure (Figure 2, right). The opposite behavior should be expected and is usually observed in the lattice structures of other amphiphilic monolayers. Above the phase transition, typical values for a rotator phase indicating free rotation of the alkyl chains are found. Below the phase transition, the small cross-sectional area indicates a drastically reduced rotation of the alkyl chains. The tilt angle t decreases remarkably at the transition. In the high pressure phase, t decreases only marginally with increasing pressure: 0.18° per mN/m at 3°C and 0.23° per mN/m at 15°C . In the low pressure phase, the tilt angle decreases more strongly with increasing pressure (0.47° per $\text{mN}\cdot\text{m}^{-1}$).

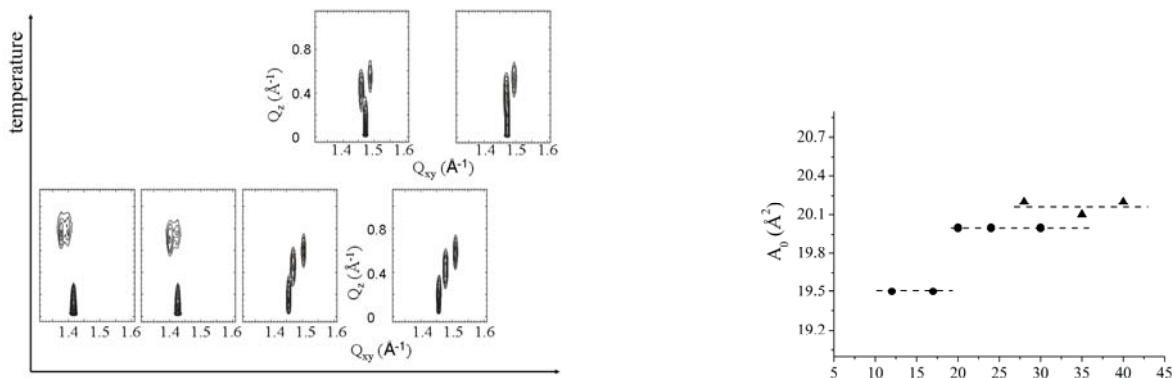


Figure 2: Left) GIXD contour plots of the corrected diffraction intensities as a function of the in-plane Q_{xy} and out-of-plane Q_z components of the scattering vectors for HTPA monolayers at different temperatures and lateral pressures: top row: 15°C , 28 and 35 mN/m (from left to right); bottom row: 3°C , 12, 18, 24 and 30 mN/m (from left to right). Right) Cross-section area of alkyl chain A_0 in dependence on the lateral pressure π at 3°C (●) and at 15°C (▲)..

References

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