

# The Phases of DODA Monolayers and the Influence of Adsorbed PSS

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We study experimentally the adsorption of polyelectrolytes onto an oppositely charged surface. As a model surface, we choose insoluble monolayers of the cationic lipid DODA (**dioctadecyldimethylammonium bromide**) at the air/water interface. In the aqueous subphase, the negatively charged polyelectrolyte PSS (**Polystyrene-sulfonate**,  $M_w=77\text{kDa}$ ) is dissolved. The electron density profile along the surface normal and the lateral structures are studied with X-ray GID (Grazing Incidence Diffraction) experiments at BW1, in the liquid surfaces set-up. On increase of the bulk concentration, more and more PSS adsorbs onto the lipid surface. At intermediate concentrations ( $10^{-6}$ - $10^{-3}$  mol/L, with respect to the monomer concentration) the two dimensional lamellar phase was found [1], which was predicted theoretically ten years ago [2]. We studied the properties of the two-dimensional lamellar phase and the parameters, which influence the chain separation. We found that the chain separation could be varied by a factor of three, by adjusting the lipid surface density and the polyelectrolyte bulk concentration [1].

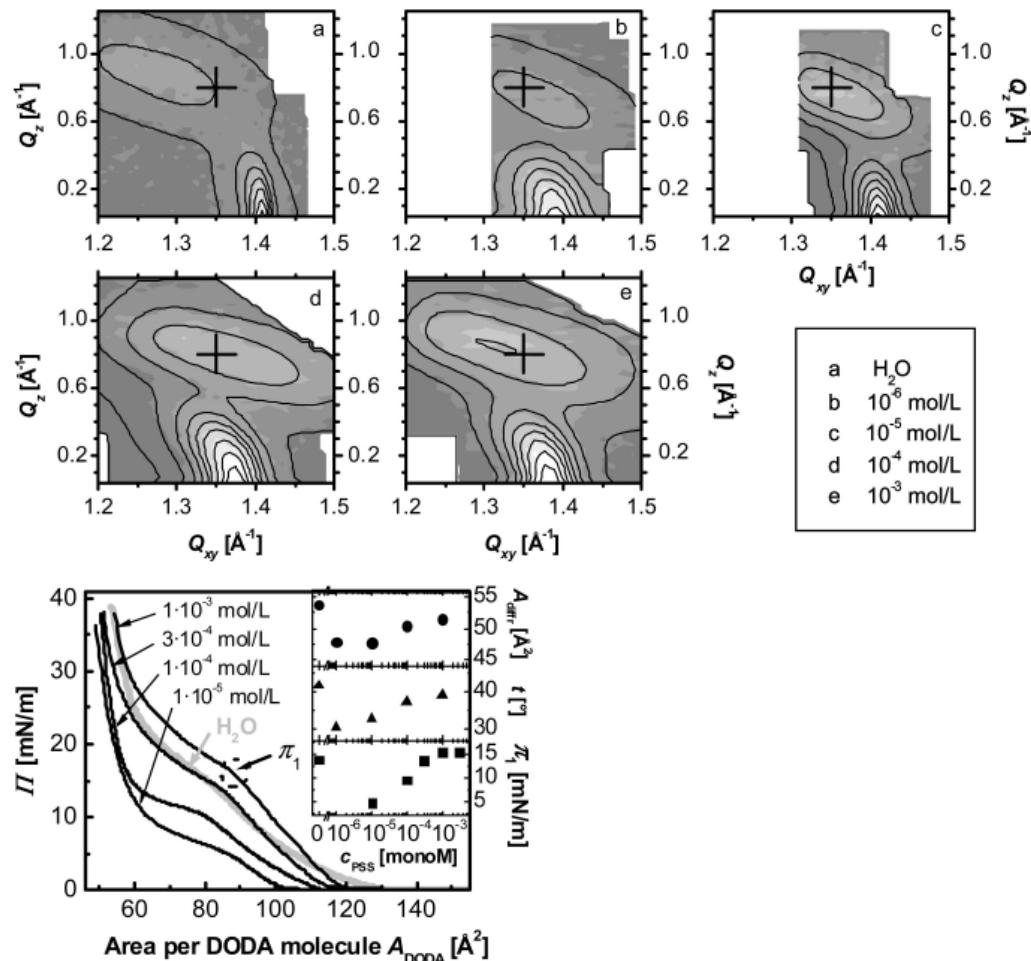


Figure 1: (Top) X-ray diffraction data from the DODA alkyl tail lattice at 30-33 mN/m on clean water and on aqueous solutions containing different PSS bulk concentrations  $c_{\text{PSS}}$ . The cross at  $(Q_{xy}, Q_z) = (1.35, 0.8)$  is given as guide to the eye, to better recognize changes in the diffraction pattern. (Bottom) Compression isotherms of DODA on pure water (bold, gray) and with various PSS concentrations. The inset shows the results from the GID measurements:  $A_{\text{diff}}$ , the area per DODA, and  $t$ , the tilt angle. Additionally, the liquid/condensed phase transition pressure  $\pi_1$  as a function of  $c_{\text{PSS}}$  is given.

From phospholipids it is known that the interplay of interactions within the monolayer and of the monolayer with adsorbed species causes a richness of lipid phases [3]. In comparison to phospholipids, the head group of DODA is much smaller, and we assume that the ordered phase is determined mainly by alkyl tail interactions. On clean water and in the condensed phase the alkyl tails of DODA form an oblique lattice. The tilt angle  $t \approx 35^\circ$  is large; the azimuth angle  $\Psi \approx 15^\circ$  has a broad distribution  $\Delta \Psi \approx 20^\circ$ . Actually, the distribution of azimuth angles causes the banana-like shape of the diffraction peak. If the order of the alkyl tail lattice (i.e. interplanar spacings, angles) is maintained in a local coordinate system perpendicular to the tail axis, changes in tilt and azimuth angles affect the peak positions. But the absolute value of the diffraction peak

is constant and peak positions should lie on the circumference of a circle (cf. Fig. 2) [4].

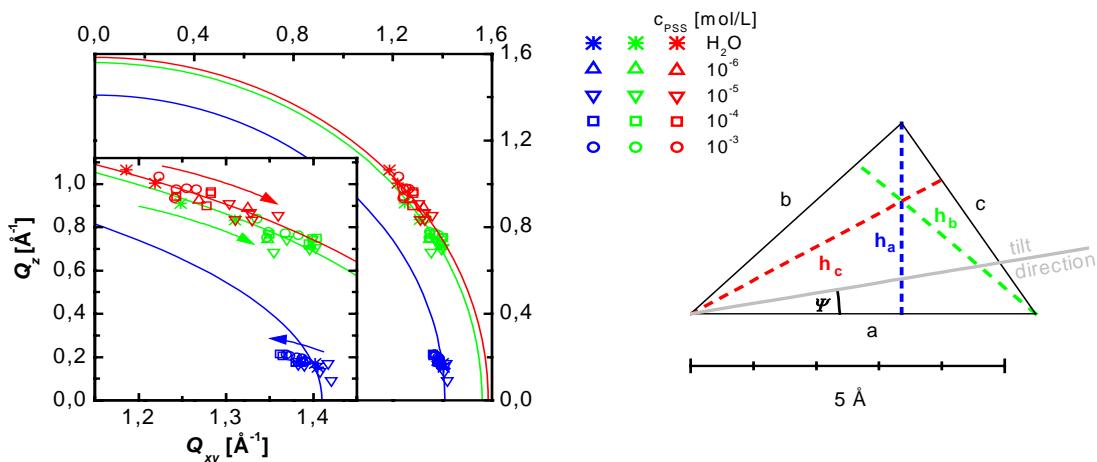


Figure 2: (Left) Peak positions for DODA alkyl tail lattice on compression (left). According to Eq. (13), the radius of the respective circles is inversely proportional to the square of the measured interplanar distance in the local coordinate system. (Right) Sketch of the lattice in the laboratory coordinate system. On transformation from the laboratory to the local coordinate system, the height  $h_a$  is least affected, since it is almost perpendicular to the tilt direction (indicated by a gray line). However, both  $h_b$  and  $h_c$  exhibit small angles relative to the tilt direction, therefore (green) and (red) are much shorter than  $h_b$  and  $h_c$ . Thus, (blue) ends up as the largest interplanar distance in the local coordinate system (even though  $h_a$  is not necessarily the largest height in the laboratory coordinate system). For the measurements shown on the left, the subphase is pure water (crosses), or PSS with different concentrations (in mol/L):  $10^{-6}$  (up triangles),  $10^{-5}$  (down triangles),  $10^{-4}$  (squares) and  $10^{-3}$  (circles). The arrows indicate changes of the peak position on monolayer compression.

Within 2%, all interplanar distances in the local coordinate system are constant (cf. Fig. 2). On monolayer compression, the tilt angle is reduced and the lateral alkyl tail density is a bit increased. At low PSS bulk concentrations ( $\leq 10^{-4}$  mol/L), the molecular area in the condensed phase as well as the surface pressure indicating the fluid/condensed phase transition are decreased (cf. Fig. 1), an effect that is attributed to PSS shielding the electrostatic repulsion of the DODA molecules. However, the alkyl tail lattice itself remains unchanged.

## References

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