Two-Dimensional Lamellar Phase of PSS Adsorbed to the Condensed Phase of Oppositely Charged TAP Monolayers in the Condensed Phase

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In a salt-free solution, electrostatic forces are large, both in amplitude and in range. Therefore, polyelectrolytes have an increased persistence length due to the electrostatic repulsion of like-charged monomers and adsorb flatly on an oppositely charged surface. This was demonstrated with lipid monolayers, and using X-ray reflectivity [1, 2]. Theoretical calculations predict a two-dimensional lamellar phase, and simultaneously charge compensation [3]. Using Grazing Incidence Diffraction (GID), this two-dimensional lamellar phase was indeed observed, the polyelectrolyte surface coverage was controlled by the concentration in the subphase [1]. Unexpected was the finding that the GID peak attributed to the aligned polyelectrolytes chains has a pronounced out-of-plane structure, with two peaks in the direction normal to film surface. The second peak was attributed to a corrugation of the film/air interface. We want to show that the two-dimensional lamellar is not limited to one type of lipid, and we want to investigate the out-of-plane structure of the GID peaks. Therefore, we use lipids (1,2-dialkoyl-3-**t**rimethyl**a**mmonium-**p**ropane, TAP) with the same head group and we vary the alkyl chain length. The chains consist either of 14, 16, or 18 carbon atoms (denominated TAP-14, TAP-16 and TAP-18, respectively). 0.01 M polystyrene sulfonate (PSS) is in the subphase. GID measurements are performed at BW1 with the liquid surfaces set-up.

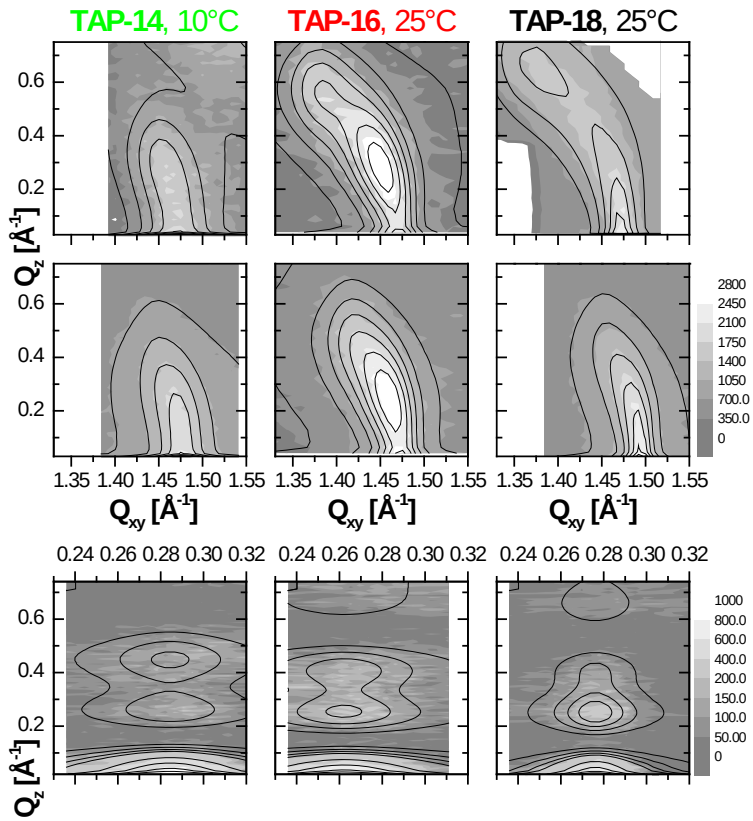

Figure 1: GID measurements of TAP monolayers with adsorbed PSS. Varied is the alkyl chain length of TAP (TAP-14 with PSS in the left column). The peaks at large Q_{xy} are due to the ordered alkyl chains of the respective lipids (top row: 20 mN/m, centre row: 40 mN/m). The peaks at low Q_{xy} measure the separation of aligned PSS chains (40 mN/m).

In the condensed phase of the lipids, GID demonstrates that the alkyl chains are tilted with respect to the surface normal. On monolayer compression, the tilt angle decreases. The low-angle GID characterizes the two-dimensional lamellar phase of PSS. Two to three higher order peaks are observed. The separation of the

PSS chains is independent of the alkyl chain length. However, with increasing alkyl chain length the higher order peaks shift to lower Q_z-values. Calculations show that the highest order Q_z peak is caused by the electron density variation at the film/air interface (cf. Fig. 2).

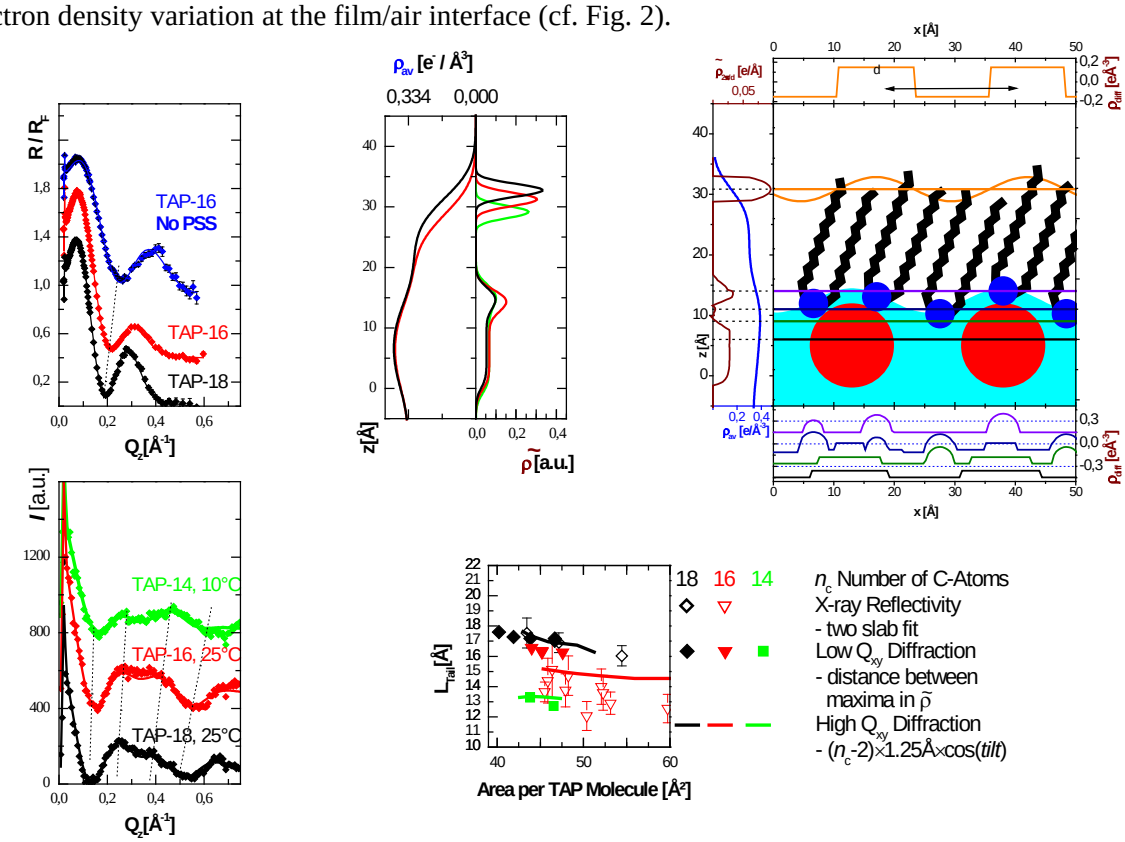

Figure 2, left, top: X-ray reflectivity curves of TAP-16 without and with adsorbed PSS; also TAP-18 with PSS. Left, bottom: Rod-scans of the GID peaks of the three lipids at 40 mN/m integrated for $0.25\ \text{Å}^{-1} \le Q_{xy} \le 0.3\ \text{Å}^{-1}$. Centre (top): Average electron density profile from the reflectivity curves (left) and vertical diffraction profile $\tilde{\rho}$ derived from the rod-scans (right). z = 0 is set at the maximum of the head groups. Right (top): Side view of TAP monolayer in the condensed phase with adsorbed PSS chains. The PSS chains are described as horizontal cylinders. Also shown are varying electron density $\rho_{diff}(x,z)$ at various heights z. Based on this model, ρ_{av} and $\tilde{\rho}$ are calculated. Right (bottom): The Thickness of the hydrophobic moiety for the different alkyl chain lengths (as indicated) is derived by different methods: Analysis of the rod-scans (full symbols), X-ray reflectivity (open symbols), and according to the molecular formula of the alkyl chains, after correction for tilt angle and C-atoms attributed to the head group (full lines).

The electron density of the monolayer is described as $\rho(x,y,z) = \rho_{av}(z) + \rho_{diff}(x,y,z)$ with $\int \rho_{diff}(x,y,z)\partial x \partial y = 0$. The laterally averaged out-of-plane electron density profile $\rho_{av}(z)$ determines the X-ray reflectivity (cf. Fig. 2). The vertical diffraction profile $\tilde{\rho}(z) = \int \rho_{diff}(x,y,z) e^{-i(Q_x x + Q_y y)} \partial x \partial y$ is obtained by a Fourier transformation. To justify a model, the out-of-plane distance between structural features should be the same according to X-ray reflectivity and GID. Varying the alkyl chain length, we find indeed a good agreement for the thickness of the hydrophobic moiety (cf. Fig. 2, right, bottom) for all three lipids with their different alkyl chain lengths. The other peaks of the low-angle GID-peak are attributed to a partial rearrangement of the lipid head groups along the PSS chains (cf. the model depicted in Fig. 2, right, top).

References

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