Alkylthio-benzoquinones and -hydroquinones: interaction with lipidic model membranes at different pH values

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Alkylthiobenzoquinones (ATQs) and the corresponding reduced alkylthiohydroquinones (ATHs) are synthetic molecules with similarities to ubiquinones (ubiquinones are involved in electron transport in mitochondria). They serve, in their reduced forms, as antioxidants and are present in all aerobic organisms, plants, animals and bacteria, but are absent from Gram-positive eubacteria and the archaebacteria.

We want to investigate their influence on the structural behaviour of phospholipid model membranes, attempting to mimic their influence on real cell membranes. The synthesised ATQs/ATHs contain a long alkylthio chain covalently attached to the ring that characterises the quinone/hydroquinone structure (Figure 1), making them amphiphilic molecules. The alkylthio chain enhances considerably the hydrophobicity of such molecules, intuitively suggesting their insertion in the phospholipids bilayer matrix, and, as a result, modifying their surface curvature.

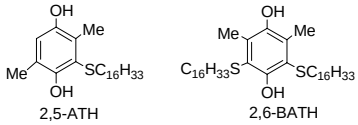

Figure 1. Example of ATHs used in this project.

Previous results on those mixtures of such ATQs/ATHs and phospholipids, investigated by X-ray scattering, have shown a very complex set of data. The observed diffraction patterns gave evidence of separation of the components into crystals of ATQs/ATHs dispersed in a lipidic medium. Different molar ratios between lipid and ATQs/ATHs did not unequivocally elucidated the observed experimental patterns, leading to a non satisfactory structural model for such system.

The formation of phospholipids basic mesostructures normally follows the hydration of dry lipid with the desired solvent/buffer. Pre-weighted amounts of lipid and ATQs/ATHs were dissolved in a defined volume of chloroform, leading to clear solutions. Pre-calculated volumes were taken and mixed into clearly homogeneous solutions. The solvent was removed and the dry homogeneous mixtures hydrated.

The SAXS measurements were carried out at the beam line A2, λ = 0.15 nm. The samples were prepared at least 24 h before measurements and left to rest at the measurement temperature for at least 5 min prior to the data acquisition.

We measured samples covering a range of interactions. Similar lipids, differing in the net charge of the polar head, POPE and POPC, were mixed with 2,6-BATH (Figure 1), a compound with two similar alkythio chains. Moreover, samples containing 2,5-ATH (with a single alkylthio chain) mixed with POPE were also investigated in order to verify the effect of the hydrophobicity of this additive on the phospholipidic bilayer.

The system investigated in more detail was POPE/2,6-BATH. It showed other structures in addition to the lamellar and hexagonal phases. The system based on POPE and 2,5-ATH, did not show more complex phases, clearly illustrating the different ability of 2,6-BATH as compared to 2,5-ATH in modifying the bilayer curvature of POPE lipids. Moreover, the analogous system based on POPC/2,6-BATH also does not show such phase.