X-ray reflectivity has been used to probe the spontaneous formation of nanoscopic films at the surface of the salt-rich phase of a PEG-potassium phosphate-water mixture. Previously, we had shown that a drop of the lighter PEG-rich phase placed on the surface of the heavier salt-rich phase would spread to form 4-nanometer thick films in coexistence with bulk droplets (1). If these very thin films are in equilibrium, it is reasonable to expect that they will spontaneously form on the surface of the salt-rich phase. We have confirmed the existence of these spontaneously formed films by studying the surface of the salt-rich phase without adding a drop of the PEG-rich phase. Studies of the film thickness as a function of salt concentration reveal an interesting crossover from 1 - 2 nanometer thick films at high concentrations to 4-nanometer thick films at lower concentration. The crossover concentration is 16 wt% salt (for fixed concentration of 13 wt% PEG). Using visual observations of the droplet spreading of PEG-rich droplets, we have also shown that this concentration corresponds to a crossover in the spreading kinetics. The connection between these two phenomena is being pursued.

References: