The monolayer characteristics of two very similar amphiphiles, 3-hydroxy-N-tridecyl propanoic acid amide (C₁₃H₂₇-NH-CO-C₂H₄OH; THPA) and tetradecanoic acid-(2-hydroxyethyl)amide (C₁₃H₂₇-CO-NH-C₂H₄-OH; TDAHA), whose chemical structure is only changed by exchanging the two substituents at the acid amide group, are compared. The main characteristics, such as surface pressure_area (\(\pi-A\)) isotherms, morphology of the condensed phase domains, lattice structure of the condensed phase, and the existence of hydrogen bonds (\(\text{—NH—O—C—}\)) of the monolayers of the highly purified amphiphiles are determined. At low temperatures (\(T \leq 10^\circ\text{C}\)), the \(\pi-A\) isotherms of both amphiphilic amides reveal a striking second critical point indicating the existence of a second phase transition between two condensed phases. This phase transition between two condensed phases is accompanied by an abrupt change of important 2D lattice parameters. Above this transition, TDAHA changes the monolayer structure from oblique to NNN tilted orthorhombic (L₂'), whereas HTPA forms another oblique phase.

Thorough GIXD studies of HTPA monolayers have revealed a new phenomenon [1]. The cross-sectional area (\(A_0\)) of the alkyl chain jumps from a smaller value in the phase at the lower surface pressure to a larger value in the phase existing at higher pressures (see Figure).

![Figure: GIXD results of the cross-section area of alkyl chain \(A_0\) in dependence on the lateral pressure \(\pi\) at 3°C (∙) and at 15 °C (▲).](image)

The opposite behaviour should be expected and is usually noted in the lattice structures of Langmuir monolayers. Computational studies, using the ab initio level of theory for the headgroup and the molecular mechanical theory for the alkyl chain part, provide a reasonable explanation for the unexpected, novel finding that the cross-sectional area of the alkyl chains jumps to larger values at the phase transition on increasing pressure. It is shown that shortening of the hydrogen bond separation at higher pressure in the headgroup region obviously drives the increase in separation between the alkyl chains, in reasonable agreement with the GIXD results.