ESRF	**Experiment title:** Influence of the Terminal Charge on the Self-Assembly or Proline-Rich Surfactant Like Peptides	**Experiment number**: MX-1769
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Report:

The surfactant-like peptide $(Ala)_6$-(Asp) (A_6D) is shown to self-assemble into ultrathin (3 nm thick) nanosheets in aqueous solution above a critical aggregation concentration.[1] The self-assembly can be modulated by addition of hexamethylene diamine which is expected to interact with the anionic C terminus (and C terminal D residue) of the peptide. Multiple ordered nanostructures can be accessed depending on the amount of added diamine. Twisted nanoribbon, nanotube, nanoplatelet and bicontinuous network structures were observed using SAXS. Addition of hexamethylene diamine at a sufficiently large molar ratio leads to disruption of ordered nanostructure and the formation of a solution of A_6D-diamine molecular complexes with highly charged end groups.

SAXS measured intensity profiles with model form factor fits are shown in Fig.1.[1] The fit parameters are listed in Table 1. The profile for 1 wt% A_6D is very similar to that previously reported for 1 wt% A_6R.[2] The data can be fitted to a "Gaussian bilayer" form factor,[3] as described elsewhere[4-6] this form factor describes the electron density profile of a planar bilayer structure with three Gaussian functions representing the electron density of the core (here: hydrophobic A residues) and two for the surfaces (here: hydrophilic D residues). Here, similar to the case of A_6R,[2] we propose that A_6D actually self-assembles into "monolayers" with a core of interdigitated A_6 chains and surfaces of D residues. This is consistent with the fact that the layer thickness is determined to be 2.9 nm, which is slightly larger than the estimated length of the chain in a parallel β-sheet (7×0.32 nm[7] = 2.2 nm) indicating interdigitation of the opposed chains. The low q part of the SAXS data for the 2:1 A_6D: diamine mixture can also be fitted using the Gaussian bilayer model. At high q, a broad Bragg peak at $q_0 = 2.9$ nm^{-1} is observed, corresponding to a structure with a periodicity $d = 2.2$ nm. This is close to the bilayer thickness obtained from the form factor fits, but identical to the estimated molecular length. Its presence suggests that some stacked layer structures exist in the 2:1 mixture solution. The spacing of the stacked layer structures is smaller than that of the nanosheets, indicating complete interdigitation of the A_6D peptide chains. This Bragg peak was not accounted for in the form factor fitting. The SAXS data for the 1:1 mixture shows a similar scaling-law type decay of the intensity at low q as for the A_6D and 2:1 mixtures (Fig.1). The Gaussian bilayer form factor was supplemented with a contribution to allow for the mesh structure. For this purpose, we used the "broad peak" function (Eq.1) to account for the presence of a broad peak in the measured SAXS data centred around $q_0 = 0.64$ nm^{-1} (Fig.1). The SAXS profile for the 1:2 A_6D: diamine solution showed a completely different shape to those for the other solutions, in particular a lack of any peak at higher q due to a bilayer form factor (Fig.1) and was not fitted to a Gaussian bilayer form factor. The SAXS profile for diamine alone (not shown) was not distinguishable from background (as expected for a dilute molecular solution).

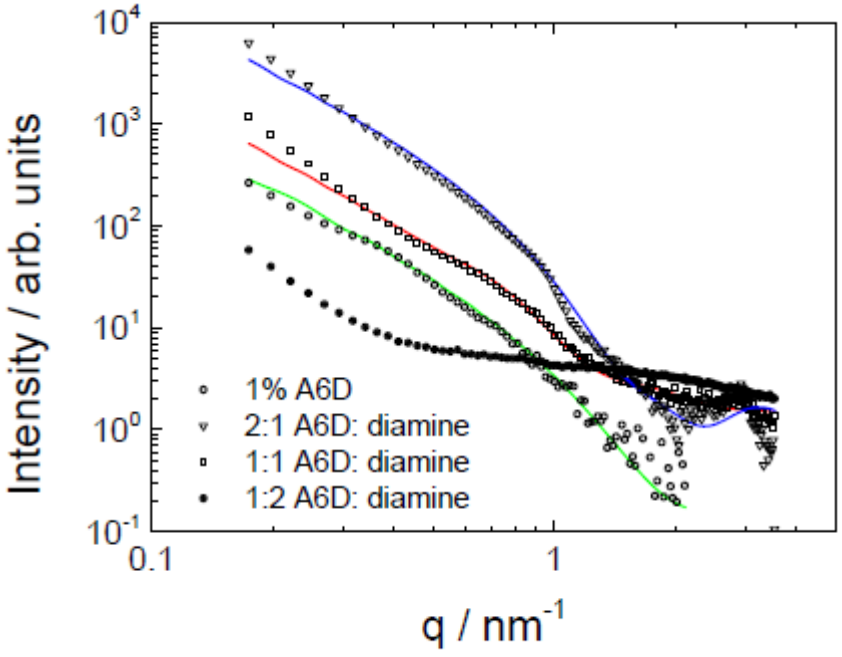

Figure 1. SAXS data (open symbols) with model form factor fits (solid lines).The fit parameters are listed in Table 1. For clarity, only every 5th measured data point is shown.[1]

Table 1. SAXS fitting parameters. [1]

Gaussian Bilayer Form Factor						
Sample	t/[a] nm	σ(core), σ(out)[b] / nm	ν(core)[c]	ν(out)[d]	Gaussian polydispersity parameters (t)[e]	Background[f]
A_6D	2.9	0.5, 0.5	0.030	0.010	N=0.20, σ=0.7	0.1
2:1 A_6D: diamine	2.9	0.3, 0.3	0.027	0.025	N=0.8, σ = 2.9	0.1
1:1 A_6D: diamine[g]	2.9	0.3, 0.3	0.0062	0.012	N=0.8, σ=0.7	1.2

[a] Bilayer thickness, [b] Width for core (lipid chain) electron density, σ_{core}, and outer (peptide) electron density, σ_{out}, Gaussian functions (fixed), [c] Scattering contrast of hydrophobic core of bilayer (with respect to solvent) (a. u.), [d] Scattering contrast of hydrophilic surface of bilayer (with respect to solvent) (a. u.), [e] Gaussian peak height N and half-width σ, [f] Radius of the bilayer (50 nm), [g] An additional "broad peak" function[3] was included in the fit due to the broad peak in the SAXS profile:

$$I(q) = \frac{I_0}{(1+(|q-q_0|\xi)^m)^p} \quad ; \; I_0 = 13.1,\ \xi = 2.7,\ q_0 = 0.64,\ m = 1.82,\ p = 1.65 \text{ fitted par.} \quad \text{(Eq. 1)}$$

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