

Supplementary material.

Structural model to describe the L₂-phase of complex salt: Swelling with increasing water or alcohol content

To make an attempt at a quantitative interpretation of the correlation distances d observed in SAXS, we use an idealized structural model of a hexagonal array of cylindrical, rod-like micelles of infinite length. A more-or-less stretched polyion is at the center of each rod, see Figure S1. The space surrounding the polyions is completely filled with water molecules, surfactant ions and alcohol molecules.

We will now consider a repeating volume element of this hexagonal structure, chosen to have a cross-sectional area given by the rhomb in Figure S1, and a height l along the direction of the rod axis. Such a rhomb is intersected by one rod, and the center-to-center distance between two neighbouring rods in the structure is d . The repeating element contains n_s surfactant ions, n_s (owing to charge neutrality) polyion repeating units, n_a alcohol molecules, and n_w water molecules. The volume of the repeating element, V_{rep} , may be expressed in terms of l and d

$$V_{rep} = (\sqrt{3}/2)d^2l \quad (S1)$$

and, also, in terms of the numbers and molar volumes of all molecules that the volume element contains

$$V_{rep} = n_s v_s + n_w v_w + n_a v_a \quad (S2)$$

where v_s , v_w and v_a are the partial molar volumes of a complex salt unit (surfactant ion plus polyion repeating unit), a water molecule and an alcohol molecule, respectively. Combining equations S1 and S2, we obtain

$$d^2 = (2/\sqrt{3})V_{rep}/l = (2/\sqrt{3})(n_s v_s + n_w v_w + n_a v_a)/l = (2/\sqrt{3})n_s v_s / l \phi_s \quad (S3)$$

Here we have, in the last equality, introduced the volume fraction ϕ_s of the complex salt

$$\phi_s = n_s v_s / (n_s v_s + n_w v_w + n_a v_a) \quad (S4)$$

The incremental increase in length of the micellar rod with each added repeating unit of the complex salt along the rod axis is

$$l_{rep} = l/n_s \quad (S5)$$

Inserting equation S5 in equation S4 we obtain

$$d^2 = (2/\sqrt{3})v_s / (l_{rep} \phi_s) \quad (S6)$$

We see that the correlation distance d in the assumed structure only depends on two variables (v_s can be assumed to be constant): the concentration of complex salt ϕ_s and the degree of stretching of the polyion inside the (infinitely long) micelle, expressed by l_{rep} .

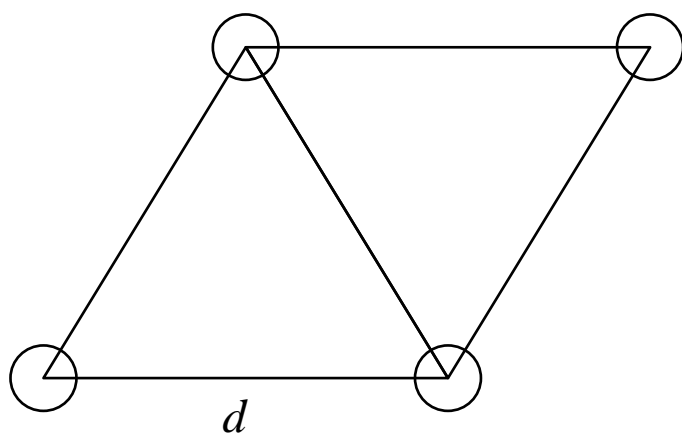


Figure S1. Representation of the hexagonal array proposed for the rod-like micelles.