Evaporation, diffusion and self-assembly at drying interfaces: Supporting Information Kevin Roger, Emma Sparr, Håkan Wennerström

S1. Calculation of the effective diffusion coefficient of water in a lamellar phase oriented perpendicularly to the evaporation flux

Assuming that the lamellar phase can be described as a stack of alternating homogeneous hydrophobic and hydrophilic layers, we can calculate the effective mutual diffusion coefficient of water perpendicular to a repetition unit of the lamellar phase as:¹

$$D_{perpendicular} = \frac{D_1 (d_1 + d_2)^2}{(d_1 + Kd_2) (d_1 + (\frac{D_1}{KD_2}) d_2)}$$
(S1)

where d_1 is the thickness of the hydrophobic layer (hydrocarbons tails), d_2 is the thickness of the hydrophilic layer (water + sugar headgroups), D_1 the diffusion coefficient of water in the hydrophobic layer, and D_2 the diffusion coefficient of water in the hydrophilic layer. The equilibrium partition coefficient of water between the hydrophilic layer and hydrophobic layer is defined as $K = \frac{c_{sugar}^{water}}{c_{tail}^{water}}$. Here, c_{sugar}^{water} is directly calculated from the experimentally known amount of water in the lamellar phase. The solubility of water in dodecane, which is an adequate model for the hydrophobic layer consisting of C₁₂ tails, is reported as $c_{dodecane}^{water} =$ 2.69 mmol/L dodecane.² This value corresponds to the solubility of water in dodecane that is in equilibrium with water. To calculate the solubility of water in dodecane that is in equilibrium with a water/sugar solution, the hydrated hydrophilic heads, we need the chemical potential variation of water between pure water this water/sugar solution. This leads to the expression of the water concentration in the tail region:

$$c_{tail}^{water} = c_{dodecane}^{water} \cdot \exp\left(\frac{\Delta \mu_{lamellar}^{water}}{_{RT}}\right)$$
(S2)

From the measured activity/composition isotherm (Figure S1), we read $-1.5 < \Delta \mu_{lamellar}^{water} < -0.2$, which then leads to: $0.6 \ mmol/L < c_{tail}^{water} < 2.2 \ mmol/L$ and thus 3350 < K < 550. Since the lamellar phase composition range is $0.018 < \phi_{lamellar}^{water} < 0.12$, and the surfactant head accounts for 49% of the surfactant volume,³ we can estimate $0.8 < d_1/d_2 < 1$ for the lamellar phase. The diffusion coefficient of water in the tail, D_1 , is taken as the self-diffusion coefficient of water in water, $2.3 \cdot 10^{-9} \ m^2/s$, the diffusion coefficient of water in the hydrophilic layer, D_2 , is taken as the diffusion coefficient of water in a concentrated sugar solution, $3.10^{-11} \ m^2/s$ (the precise value of D_2 has in practice no quantitative consequences on the outcome of the calculations). Together, this leads to an estimate of the diffusion coefficient according to Eqn (S1):

$$1.6.10^{-12}m^2/s < D_{perpendicular} < 2.6.10^{-12}m^2/s$$
 (S3)

S2. Activity/Composition isotherm of water and surfactant

We measured the activity/composition isotherm for water at 23°C using sorption calorimetry (Figure S1, top),⁴ where the water activity, a_{w} , is directly related to the chemical potential of water, $\Delta \mu_w$, as

 $\Delta \mu_w = RT \ln a_w$

Since this is a purely binary system, the surfactant activity/composition isotherm can be recalculated from the water activity/composition isotherm using the Gibbs-Duhem relationship. The result is shown (Figure S1) below together with an extrapolation to conditions with low surfactant concentration. The sorption calorimetry method does not provide accurate measurements for high water activities (low surfactant concentration), which limits the precision of the calculations for this concentration regime (determination of the effective mutual diffusion coefficient in the micellar cubic phase, for instance).





S3. Derivation of eqn 10 using a variable transformation

The equation of continuity results in

$$\frac{\partial \phi}{\partial t} = -\frac{\partial J(z,t)}{\partial z} = -\nu \frac{\partial \phi}{\partial z} + \frac{\partial \left\{ \frac{D(\phi)}{RT} \phi \frac{\partial \mu \partial \phi}{\partial \phi \partial z} \right\}}{\partial z}$$
(8)

where the net flow of the solute, J(z, t), is then given by eqn (6), and the advective liquid flow is

$$v(t) = -D(\phi_0) \{ \frac{d\mu}{d\phi} \frac{\partial\phi}{\partial z} \}_{z=0} / RT$$
(9)

The partial differential eqn (8) can be transformed into an ordinary differential equation by introducing the variable transformation to a dimensionless parameter *x*,

$$x = z/\sqrt{D_0 t} \qquad (t \neq 0) \tag{3}$$

where D_0 is the diffusion coefficient of pure water. The partial derivatives of x with respect to z and t are expressed as

$$\frac{\partial x}{\partial t} = \frac{-z}{2t\sqrt{D_0 t}} = -\frac{x}{2t} \tag{S5}$$

and

$$\frac{\partial x}{\partial z} = \frac{1}{\sqrt{D_0 t}} \tag{S6}$$

The left hand side of eqn (8) can be rewritten using the variable transformation (3 and S5), giving

$$\frac{\partial \Phi}{\partial t} = \frac{\partial \Phi}{\partial x} \frac{\partial x}{\partial t} = -\frac{x}{2} \frac{\partial \Phi}{\partial x} \cdot \frac{1}{t}$$
(S7)

Using the same variable transformation (3 and S6), the first term of the right hand side of eqn (8) can be written as

$$v\frac{\partial\Phi}{\partial z} = -\frac{D(\Phi_0)}{RT} \left\{ \frac{\partial\mu}{\partial\Phi} \frac{\partial\Phi}{\partial z} \right\}_{z=0} \cdot \frac{\partial\Phi}{\partial z} = -\frac{D(\Phi_0)}{RT} \frac{1}{\sqrt{D_0 t}} \left\{ \frac{\partial\mu}{\partial\Phi} \frac{\partial\Phi}{\partial x} \right\}_{x=0} \cdot \frac{1}{\sqrt{D_0 t}} \frac{\partial\Phi}{\partial x} = -\frac{1}{c_0} \cdot \left\{ \frac{\partial\Phi}{\partial x} \right\}_{x=0} \cdot \frac{\partial\Phi}{\partial x} \cdot \frac{1}{t}$$
(S8)

where C₀ is defined as

$$1/C_0 \stackrel{\text{def}}{=} \frac{D(\phi_0)}{D_0 RT} \left\{ \frac{d\mu}{d\phi} \right\}_{\phi = \phi_0} \tag{S9}$$

and the second term at the right hand in eq 8 can be written as

$$\frac{\partial}{\partial z} \left\{ \frac{D(\Phi)}{RT} \Phi \frac{\partial \mu}{\partial \Phi} \frac{\partial \Phi}{\partial z} \right\} = \frac{\partial}{\partial z} \left\{ \frac{D(\Phi)}{\sqrt{D_0 t_{RT}}} \Phi \frac{\partial \mu}{\partial \Phi} \frac{\partial \Phi}{\partial x} \right\} = \frac{\partial}{\partial x} \left\{ \frac{D(\Phi)}{D_0 RT} \Phi \frac{\partial \mu}{\partial \Phi} \frac{\partial \Phi}{\partial x} \right\} \cdot \frac{1}{t} = \frac{\partial}{\partial x} \left\{ f_s(\Phi) \frac{\partial \Phi}{\partial x} \right\} \cdot \frac{1}{t} = \left\{ \frac{\partial f_s}{\partial x} \left(\frac{\partial \Phi}{\partial x} \right)^2 + f_s(\Phi) \frac{\partial^2 \Phi}{\partial x^2} \right\} \cdot \frac{1}{t}$$
(S10)

where $f_s(\Phi)$ is defined as

$$f_{S}(\phi) \stackrel{\text{def}}{=} \frac{D(\phi)}{D_{0}RT} \phi \frac{d\mu}{d\phi}$$
(S11)

Combining eqn 8, S7, S8, and S10 finally gives

$$-\frac{x}{2}\frac{\partial\Phi}{\partial x} = -\frac{1}{c_0} \cdot \left\{\frac{\partial\Phi}{\partial x}\right\}_{x=0} \cdot \frac{\partial\Phi}{\partial x} + \left(\frac{\partial\Phi}{\partial x}\right)^2 \frac{\partial f_s}{\partial x} + f_s(\Phi) \frac{\partial^2\Phi}{\partial x^2}$$
(10)

S4. Mesostructure characterization using SAXS



lamellar hexagonal micellar cubic micellar

Figure S2 : Several mesophases are observed along the concentration gradient extending from the capillary's tip to the reservoir (a). We characterized these mesostructures using SAXS. Two dimensional pattern were observed and displayed anisotropy for the lamellar and hexagonal phases, which shows that these phases are oriented in the capillary setup (b). Azimuthal integration was performed to obtain structure maps, which give the peak positions for the different mesophases (c). From the peak sequence, we can deduce the mesostructure (d).

References

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