

INVESTIGATION OF THE ENHANCED ABILITY OF BILE SALT SURFACTANTS TO SOLUBILIZE PHOSPHOLIPID BILAYERS AND FORMING MIXED MICELLES

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Derivation of bending elasticity constants for self-assembled monolayers formed by surfactants with rigid and flexible tail

We may write the free energy per unit area as a function of the mean and Gaussian curvatures, H and K , respectively, in accordance with the Helfrich expression ¹

$$\gamma(H,K) = \gamma_0 + 2k_c(H - H_0)^2 + \bar{k}_c K = \gamma_p - 4k_c H_0 H + 2k_c H^2 + \bar{k}_c K \quad (S1)$$

Eq (S1) introduces three bending elasticity constants, *i.e.* spontaneous curvature ($k_c H_0$), bending rigidity (k_c) and saddle-splay constant (\bar{k}_c). $\gamma_p = \gamma(H = K = 0)$ is the free energy per unit area of a planar monolayer whereas $\gamma_0 = \gamma_p - 2k_c H_0^2$ denotes the corresponding quantity at $H = H_0$ and $K = 0$. Hence, the three bending elasticity constants may formally be defined as

$$k_c H_0 = -\frac{1}{4} \left(\frac{\partial \gamma}{\partial H} \right)_K [H = 0] \quad (S2)$$

$$k_c = \frac{1}{4} \left(\frac{\partial^2 \gamma}{\partial H^2} \right)_K [H = 0] \quad (S3)$$

$$\bar{k}_c = \left(\frac{\partial \gamma}{\partial K} \right)_H [K = 0] \quad (S4)$$

where $\gamma = \varepsilon/a$ and ε is the free energy and a the area per aggregated surfactant.

Surfactants with rigid tails

We may write the three bending elasticity constants as sums of the three contributions hydrophobic effect (hb), electrostatic free energy (el) and residual head group free energy (hg) ^{2,3}, *i.e.*

$$k_c H_0 = (k_c H_0)_{hb} + (k_c H_0)_{hg} + (k_c H_0)_{el} \quad (S5)$$

$$k_c = k_c^{hb} + k_c^{hg} + k_c^{el} \quad (S6)$$

$$\bar{k}_c = \bar{k}_c^{hb} + \bar{k}_c^{hg} + \bar{k}_c^{el} \quad (S7)$$

We may also write the area per aggregated surfactant, a , as an expansion in H and K ,

$$\frac{1}{a} = \frac{1}{a_p} (1 + k_a' H + k_a'' H^2 + k_a''' K) \quad (\text{S8})$$

where lower case p denotes planar geometry and k_a', k_a'', k_a''' are three constants with respect to curvature.

The hydrophobic effect

The hydrophobic free energy per aggregated surfactant

$$\varepsilon_{hb} = \varepsilon_{hb}^\circ + a\gamma_{hb} \quad (\text{S9})$$

where γ_{hb} is the hydrocarbon/water interfacial tension. Combining Eqs (S8) and (S9), and identifying $\gamma = \varepsilon/a$ with the Helfrich expression in Eq (S1), gives ²

$$(k_c H_0)_{hb} = \frac{\gamma_{hb} k_a'}{4} \quad (\text{S10})$$

$$k_c^{hb} = -\frac{\gamma_{hb} k_a''}{2} \quad (\text{S11})$$

$$k_c^{hb} = -\gamma_{hb} k_a''' \quad (\text{S12})$$

Electrostatics

The curvature dependence on the electrostatic free energy as calculated from the Gouy-Chapman solution to the Poisson-Boltzmann-equation has previously been derived by Mitchel and Ninham ⁴, *i.e.*

$$\frac{\varepsilon_{el}}{kT} = h_0 + h_1 H_{el} + h_2 H_{el}^2 + h_3 K_{el} \quad (\text{S13})$$

where H_{el} and K_{el} are defined at the surface of charge, k is Boltzmann's constant and T is the absolute temperature. The four parameters

$$h_0 = 2[\ln(S + \sqrt{S^2 + 1})] - \frac{\sqrt{S^2 + 1} - 1}{S} \quad (S14)$$

$$h_1 = -\frac{4}{\kappa S} \ln\left(\frac{1 + \sqrt{S^2 + 1}}{2}\right) \quad (S15)$$

$$h_2 = \frac{2}{\kappa^2 S} \left(1 - \frac{2}{S^2} + \frac{2}{S^2 \sqrt{S^2 + 1}}\right) \quad (S16)$$

$$h_3 = -\frac{2}{\kappa^2 S} D_1\left(\ln\left(\frac{1 + \sqrt{S^2 + 1}}{2}\right)\right) \quad (S17)$$

are functions of the reduced charge density S and the Debye screening length κ^{-1} . D_1 denotes the Debye function, defined as

$$D_1(x) = \int_0^x \frac{t}{e^t - 1} dt \quad (S18)$$

Assuming the surface of charge to be located a distance $d/2$ outside the hydrocarbon/water interface (corresponding to the center of a spherical head group with diameter d), the following expressions may be derived from Eqs (S2-4), (S8) and (S13)

$$\frac{(k_c H_0)_{el}}{kT} = \frac{1}{2\pi l_B} \ln\left(\frac{S_p}{2q}\right) + \frac{q}{2a_p} (d - k'_a) \quad (S19)$$

$$\frac{k_c^{el}}{kT} = \frac{\kappa^{-1}}{2\pi l_B} \left(1 - \frac{2(p-q)^2}{pq}\right) + \frac{pq}{\pi l_B} (d - k'_a) + \frac{p}{2a_p} (d - k'_a)^2 + \frac{q}{a_p} k''_a \quad (S20)$$

$$\frac{k_c^{el}}{kT} = -\frac{\kappa^{-1}}{\pi l_B} D_1\left(\ln\left(\frac{S_p}{2q}\right)\right) - \frac{d}{\pi l_B} \ln\left(\frac{S_p}{2q}\right) - \frac{2q}{a_p} \left(\frac{d^2}{4} - k'''_a\right) \quad (S21)$$

We have introduced the dimensionless parameters

$$p = \frac{S_p}{\sqrt{S_p^2 + 1}} \quad (\text{S22})$$

$$q = \frac{S_p}{\sqrt{S_p^2 + 1} + 1} = \frac{\sqrt{S_p^2 + 1} - 1}{S_p} \quad (\text{S23})$$

which both assume values between zero and unity and where the reduced surface charge density is defined as

$$S_p = \frac{2\pi l_B}{\kappa a_p} \quad (\text{S24})$$

where $l_B = 7.15 \text{ \AA}$ is the Bjerrum length and a_p is the area per molecule in a planar surfactant layer.

Head group repulsion

The free energy of mixing head groups with aqueous solvent in an outer hydrophilic shell of the surfactant layer may be written as follows ³

$$\frac{\varepsilon_{hg}}{kT} = \frac{\varepsilon_{hg}^\circ}{kT} + \frac{v_{hg}(1 - \phi_{hg})}{v_w \phi_{hg}} \ln(1 - \phi_{hg}) + \ln \phi_{hg} \quad (\text{S25})$$

where ϕ_{hg} is the volume fraction of the head groups in the shell, v_{hg} and v_w is the volumes of head group and water molecule respectively. The parameter ε_{hg}° comprises curvature independent residual contributions to the head group free energy. Because of geometrical reasons ϕ_{hg} depends on the curvature of the surfactant layer and, as a result, we have been able to derive the following expressions for the three bending elasticity constants ³

$$\frac{(k_c H_0)_{hg}}{kT} = \frac{\omega}{4a_p} (d - k'_a) \quad (\text{S26})$$

$$\frac{k_c^{hg}}{kT} = \frac{\varphi}{4a_p}(d - k_a')^2 + \frac{\omega}{2a_p}k_a'' \quad (\text{S27})$$

$$\frac{k_c^{hg}}{kT} = -\frac{\omega}{a_p}\left(\frac{d^2}{3} - k_a'''\right) \quad (\text{S28})$$

In the derivation, we have considered the head group to be a sphere with diameter d . φ and ω are two dimensionless parameters defined as

$$\varphi = 1 + \frac{v_{hg} \phi_{hg}^p}{v_w 1 - \phi_{hg}^p} \quad (\text{S29})$$

$$\omega = 1 - \frac{v_{hg}}{v_w} \left(1 + \frac{\ln(1 - \phi_{hg}^p)}{\phi_{hg}^p}\right) = 1 + \frac{v_{hg}}{v_w} \phi_{hg}^p \left(\frac{1}{2} + \frac{\phi_{hg}^p}{3} + \frac{\phi_{hg}^{p^2}}{4} + \dots\right) \quad (\text{S30})$$

where superscript p denotes planar geometry.

Spontaneous curvature

Summing the three contributions in Eqs (S10), (S19) and (S26) gives the following expression for the spontaneous curvature for a surfactant with a rigid tail

$$\left(\frac{k_c H_0}{kT}\right)_{rigid} = \frac{1}{2\pi l_B} \ln\left(\frac{S_p}{2q}\right) + \frac{d}{4a_p}(\omega + 2q) \quad (\text{S31})$$

In the derivation of (S31), we have been able to eliminate all parameters depending on k_a' through the equilibrium condition for planar geometry, *i.e.*

$$\frac{d\varepsilon_p}{da_p} = \gamma_{hb} - \frac{kT}{a_p}(\omega + 2q) = 0 \quad (\text{S32})$$

where $\varepsilon_p = \varepsilon_{hb}^p + \varepsilon_{el}^p + \varepsilon_{hg}^p$ and

$$\varepsilon_{hb}^p = \varepsilon_{hb}^\circ + a_p \gamma_{hb} \quad (\text{S33})$$

$$\frac{\varepsilon_{hg}^p}{kT} = \frac{\varepsilon_{hg}^\circ}{kT} + \frac{v_{hg}1 - \phi_{hg}^p}{v_w \phi_{hg}^p} \ln(1 - \phi_{hg}^p) + \ln \phi_{hg}^p \quad (\text{S34})$$

$$\frac{\varepsilon_{el}^p}{kT} = 2 \ln(S_p + \sqrt{S_p^2 + 1}) - q \quad (\text{S35})$$

Subscript/superscript p denoted planar geometry, *i.e.* $H = K = 0$, and superscript \circ denotes curvature independent contribution.

We may rewrite Eq (S31) by solving a_p from Eq (S32)

$$a_p = \frac{kT}{\gamma_{hb}}(\omega + 2q) \quad (\text{S36})$$

Inserting Eqs (S36) in Eq (S31) gives

$$\left(\frac{k_c H_0}{kT}\right)_{rigid} = \frac{1}{2\pi l_B} \ln\left(\frac{S_p}{2q}\right) + \frac{\gamma_{hb} d}{4kT} \quad (\text{S37})$$

We note that the first term in Eq (S37) is identical to the electrostatic contribution for an infinitely thin charged layer as derived by Mitchell and Ninham. The second term in Eq (S37) only appears as a result of the outer hydrophilic layer having a finite thickness, *i.e.* it consists of spherical head groups with a diameter d and a surface of charge located at a distance $d/2$ outside the hydrophobic-hydrophilic interface (in the central plane of the spherical head groups). We may also note that the spontaneous curvature for a surfactant with a rigid tail does not explicitly depend on the thickness ξ of the hydrophobic part of the surfactant monolayer.

Bending rigidity

Summing Eqs (S11), (S20) and (S27), as well as eliminating terms including k_a'' by means of employing the equilibrium condition in Eq (S32), gives

$$\left(\frac{k_c}{kT}\right)_{rigid} = \frac{\kappa^{-1}}{2\pi l_B} \left(1 - \frac{2(p-q)^2}{pq}\right) + \frac{pq}{\pi l_B} (d - k_a') + \frac{p}{2a_p} (d - k_a')^2 + \frac{\varphi}{4a_p} (d - k_a')^2 \quad (\text{S38})$$

This expression may be further simplified by minimizing with respect to $(d - k'_a)$ which gives

$$(d - k'_a) = -\frac{2a_p pq}{\pi l_B (\varphi + 2p)} \quad (\text{S39})$$

Inserting Eq (S39) in (S38) gives

$$\left(\frac{k_c}{kT}\right)_{rigid} = \frac{\kappa^{-1}}{2\pi l_B} \left(1 - \frac{2(p-q)^2}{pq}\right) - \frac{a_p (pq)^2}{(\pi l_B)^2 (\varphi + 2p)} \quad (\text{S40})$$

Eliminating a_p by inserting Eq (S36) in (S40) finally gives

$$\left(\frac{k_c}{kT}\right)_{rigid} = \frac{\kappa^{-1}}{2\pi l_B} \left(1 - \frac{2(p-q)^2}{pq}\right) - \left(\frac{pq}{\pi l_B}\right)^2 \frac{kT (\omega + 2q)}{\gamma_{hb} (\varphi + 2p)} \quad (\text{S41})$$

Similar to the expression for the spontaneous curvature in Eq (S37), the bending rigidity for a surfactant with rigid tail does not depend on the thickness of the hydrophobic part of the monolayer.

Saddle-splay constant

Similarly to spontaneous curvature and bending rigidity we may arrive at an expression for the saddle-splay constant by summing Eqs (S12), (S21) and (S28) as well as eliminating terms including k''_a by employing the equilibrium expression in Eq (S32)

$$\left(\frac{k_c}{kT}\right)_{rigid} = -\frac{1}{\pi l_B} \left[\kappa^{-1} D_1 \left(\ln \left(\frac{S_p}{2q} \right) \right) + d \ln \left(\frac{S_p}{2q} \right) \right] - \frac{d^2}{2a_p} \left(q + \frac{2\omega}{3} \right) \quad (\text{S42})$$

Eq (S42) may be rewritten by using Eq (S32)

$$\left(\frac{k_c}{kT}\right)_{rigid} = -\frac{1}{\pi l_B} \left[\kappa^{-1} D_1 \left(\ln \left(\frac{S_p}{2q} \right) \right) + d \ln \left(\frac{S_p}{2q} \right) \right] - \frac{\gamma_{hb} d^2}{6kT} \left(\frac{2\omega + 3q}{\omega + 2q} \right) \quad (\text{S43})$$

As for the spontaneous curvature, the expression for the saddle-splay constant in Eq (S43) may be divided into an infinitely thin monolayer contribution due to electrostatics and one finite size contribution depending on the thickness d of the hydrophilic part of the monolayer. $(k_c/kT)_{rigid}$ does not depend on the thickness ξ of the hydrophobic part of the monolayer.

Surfactants with flexible tails

Surfactants or phospholipids with one nor two flexible aliphatic chains as tail group mainly differ from surfactants with rigid tails so far as an additional free energy contribution (ε_{chain}) taking into account that chain conformational entropy must be added. ^{5, 6} ε_{chain} differs from the other contributions in the sense that it presupposes a finite thickness ξ of the hydrophobic part of the monolayer and the corresponding contribution to the spontaneous curvature can be written as ²

$$(k_c H_0)_{chain} = - \frac{\xi_p}{4a_p} \frac{d\varepsilon_{chain}^p}{d\xi_p} (\xi_p + k_a') \quad (S44)$$

From the geometrical relation $v_{tail} = \xi_p a_p$, it follows that

$$\frac{d\varepsilon_{chain}^p}{da_p} = - \frac{\xi_p}{a_p} \frac{d\varepsilon_{chain}^p}{d\xi_p} \quad (S45)$$

which gives the equilibrium condition

$$\frac{d\varepsilon_p}{da_p} = \gamma_{hb} - \frac{\omega kT}{a_p} - \frac{2qkT}{a_p} - \frac{\xi_p}{a_p} \frac{d\varepsilon_{chain}^p}{d\xi_p} = 0 \quad (S46)$$

Combining Eq (S44) and (S46) gives the following relation for chain conformational entropy contribution to the spontaneous curvature

$$(k_c H_0)_{chain} = - \frac{1}{4} \left[\gamma_{hb} - \frac{(\omega + 2q)kT}{a_p} \right] (\xi_p + k_a') \quad (S47)$$

Summing all contributions in Eqs (S10), (S19), (S26) and (S44), and eliminating terms including k_a' by means of employing the equilibrium condition in Eq (S46) gives

$$\left(\frac{k_c H_0}{kT}\right)_{flex} = \frac{1}{2\pi l_B} \ln\left(\frac{S_p}{2q}\right) + \frac{(\xi_p + d)}{4a_p}(\omega + 2q) - \frac{\xi_p \gamma_{hb}}{4kT} \quad (S48)$$

We note that, in contrast to the case of surfactants with rigid tail, the spontaneous curvature of surfactants with flexible tail depends strongly on the thickness ξ_p of the hydrophobic part of the monolayer. We may combine Eqs (S31) and (S48) to arrive at

$$\left(\frac{k_c H_0}{kT}\right)_{flex} = \left(\frac{k_c H_0}{kT}\right)_{rigid} - \frac{\xi_p}{4} \left(\frac{\gamma_{hb}}{kT} - \frac{\omega + 2q}{a_p}\right) = \left(\frac{k_c H_0}{kT}\right)_{rigid} - \frac{\xi_p^3}{4\nu kT} \frac{d\varepsilon_{chain}^p}{d\xi_p} \quad (S49)$$

Since the derivative $d\varepsilon_{chain}^p/d\xi_p$ is expected to be positive for monolayers with ξ_p larger than half the length of a fully stretched chain, we may conclude that surfactants with flexible tail are, in general, expected to have lower spontaneous curvature than surfactants with rigid tail.

Bending rigidity

The chain conformational entropy contribution to the bending rigidity is given by

$$k_c^{chain} = \frac{\xi_p^2}{4a_p} \frac{d^2\varepsilon_{chain}^p}{d\xi_p^2} (\xi_p + k_a')^2 + \frac{\xi_p}{4a_p} \frac{d\varepsilon_{chain}^p}{d\xi_p} (k_a'' + 2\xi_p k_a' + 2\xi_p^2) + \frac{\xi_p}{2a_p} \frac{d\varepsilon_{chain}^p}{d\xi_p} k_a' (\xi_p + k_a') \quad (S50)$$

Summing over the different contributions in Eqs (S11), (S20), (S27) and (S50) gives

$$\begin{aligned} \left(\frac{k_c}{kT}\right)_{flex} &= \frac{\kappa^{-1}}{2\pi l_B} \left(1 - \frac{2(p-q)^2}{pq}\right) + \frac{pq}{\pi l_B} (d - k_a') + \frac{(\varphi + 2p)}{4a_p} (d - k_a')^2 + \frac{\xi_p (\xi_p + k_a')}{2a_p} \left(\frac{a_p \gamma_{hb}}{kT} - \omega - 2\right) \end{aligned} \quad (S51)$$

Again, we have been able to eliminate terms with the parameter k_a'' by means of employing the equilibrium condition in Eq (S46). Analogous to the case with rigid surfactants, Eq (S51) may be further simplified by minimizing with respect to k_a' . However, it turns out that the chain conformational entropy contribution tends to make the thickness ξ of the surfactant monolayer rather insensitive towards changes in curvature. As a result, Eq (S51) may be approximated with the expression valid for the special case of a monolayer that is bent at constant $\xi = \xi_p$. For the latter case $k_a' = -\xi_p$ holds exactly true ² and we may simplify Eq (S51) so as to give

$$\left(\frac{k_c}{kT}\right)_{flex} = \frac{\kappa^{-1}}{2\pi l_B} \left(1 - \frac{2(p-q)^2}{pq}\right) + \frac{pq}{\pi l_B} (\xi_p + d) + \frac{(\varphi + 2p)}{4a_p} (\xi_p + d)^2 \quad (S52)$$

Combining Eqs (S41) and (S52) gives

$$\left(\frac{k_c}{kT}\right)_{flex} = \left(\frac{k_c}{kT}\right)_{rigid} + \left(\frac{pq}{\pi l_B}\right)^2 \frac{kT(\omega + 2q)}{\gamma_{hb}(\varphi + 2p)} + \frac{pq}{\pi l_B} (\xi_p + d) + \frac{(\varphi + 2p)}{4a_p} (\xi_p + d)^2 \quad (S53)$$

Analogous to the spontaneous curvature in Eq (S48), and in contrast to the case of surfactants with rigid tail, $(k_c/kT)_{flex}$ depends strongly on ξ_p . Since all parameters in the second and third terms on the right hand side of Eq (S53) are positive quantities, we may conclude that

$$\left(\frac{k_c}{kT}\right)_{flex} > \left(\frac{k_c}{kT}\right)_{rigid} \quad (S54)$$

is always true.

Saddle Splay-constant

The chain conformational entropy contributions to the saddle-splay constant equals

$$k_c^{chain} = \frac{\xi_p d \varepsilon_{chain}^p}{a_p d \xi_p} \left(k_a''' - \frac{\xi_p^2}{3} \right) \quad (S55)$$

Summing Eqs (S12), (S21), (S28) and (S55) gives

$$\left(\frac{\bar{k}_c}{kT}\right)^{flex} = -\frac{1}{\pi l_B} \left[\kappa^{-1} D_1 \left(\ln \left(\frac{S_p}{2q} \right) \right) + d \ln \left(\frac{S_p}{2q} \right) \right] - \frac{\xi_p^2}{3} \left(\frac{\gamma_{hb}}{kT} - \frac{\omega + 2q}{a_p} \right) - \frac{d^2}{2a_p} \left(q + \frac{2\omega}{3} \right) \quad (S56)$$

where all terms including k_a''' have been eliminated with the equilibrium condition in Eq (S46).

Combining Eqs (S43) and (S56) gives the following relation

$$\left(\frac{\bar{k}_c}{kT}\right)^{flex} = \left(\frac{\bar{k}_c}{kT}\right)^{rigid} - \frac{\xi_p^2}{3} \left(\frac{\gamma_{hb}}{kT} - \frac{\omega + 2q}{a_p} \right) = \left(\frac{\bar{k}_c}{kT}\right)^{rigid} - \frac{\xi_p^4}{3\nu kT} \frac{d\varepsilon_{chain}^p}{d\xi_p} \quad (S57)$$

between the saddle-splay constant for surfactants with rigid and flexible tail, respectively.

Model employed in the least squares fitting data analysis

The differential scattering cross section as a function of scattering vector q for a sample of weakly interacting monodisperse micelles with concentration n (number of micelles per unit volume) can be written as follows ⁷

$$\frac{d\sigma(q)}{d\Omega} = n(\Delta\rho_{core}V_{core})^2P(q)[1 + \beta(q)(S(q) - 1)] \quad (S58)$$

The micelles were best fitted using a form factor $P(q)$ for core-and-shell triaxial core-shell ellipsoids with half axes a , b and c of the core and a thickness d of the outer shell. In accordance, we may write the orientationally averaged form factor for a non-spherical micelle as

$$P(q) = \langle F^2(q) \rangle = \frac{2}{\pi} \int_0^{\pi/2} \int_0^{\pi/2} F(q, \phi, \theta)^2 \sin \phi d\phi d\theta \quad (S59)$$

where F is the amplitude of the form factor and

$$\beta(q) = \frac{\langle F(q) \rangle^2}{\langle F^2(q) \rangle} \quad (S60)$$

where

$$\langle F(q) \rangle = \frac{2}{\pi} \int_0^{\pi/2} \int_0^{\pi/2} F(q, \phi, \theta) \sin \phi d\phi d\theta \quad (S61)$$

For a core-and-shell micelle we may write the amplitude as a sum of contributions from the core and the shell, respectively,

$$F(q, \phi, \theta) = F_{core}(q, \phi, \theta) + \rho \frac{V_{shell}}{V_{core}} F_{shell}(q, \phi, \theta) \quad (S62)$$

where

$$q = \frac{\Delta\rho_{shell}}{\Delta\rho_{core}} \quad (S63)$$

and $\Delta\rho_{core}$ and $\Delta\rho_{shell}$ are the differences in scattering length densities between core and shell, respectively, and solvent. $V_{core} = V(a, b, c)$ is the volume of the core and $V_{shell} = V(a + d, b + d, c + d) - V(a, b, c)$ is the volume the outer shell.

The amplitude as a function of the radial distance r for a general ellipsoid with half axes a, b and c equals ⁸

$$F_{core}(q, r(a, b, c, \phi, \theta)) = F_{sph} \quad (S64)$$

where

$$F_{sph} = \frac{3[\sin(qr) - qr\cos(qr)]}{(qr)^3} \quad (S65)$$

with

$$r(a, b, c, \phi, \theta) = \sqrt{(a^2 \sin^2 \theta + b^2 \cos^2 \theta) \sin^2 \phi + c^2 \cos^2 \phi} \quad (S66)$$

The corresponding quantity for the shell may be written as

$$F_{shell} = \frac{V_{tot} F_{sph}(q, r(a + d, b + d, c + d, \phi, \theta)) - V_{core} F_{sph}(q, r(a, b, c, \phi, \theta))}{V_{shell}} \quad (S67)$$

where $V_{tot} = V(a + d, b + d, c + d) = V_{core} + V_{shell}$ and

$$r(a + d, b + d, c + d, \phi, \theta) = \sqrt{((a + d)^2 \sin^2 \theta + (b + d)^2 \cos^2 \theta) \sin^2 \phi + (c + d)^2 \cos^2 \phi} \quad (S68)$$

The parameters in the model were optimized by means of conventional least squares analysis, with the reformulation that, $a_1 = n(\Delta\rho_{core}V_{core})^2$, was used as one common scale parameter.^{7, 9} The quality of the fits were measured in terms of the reduced chi-squared parameter defined as

$$\chi^2 = \frac{1}{N - M} \sum_{i=1}^N \left(\frac{I_{exp}(q_i) - I_{mod}(q_i)}{\sigma_i} \right)^2 \quad (\text{S69})$$

where $I_{exp}(q_i)$ and $I_{mod}(q_i)$ are the experimental and model intensities, respectively, at a scattering vector modulus q_i , σ_i is the statistical uncertainties on the data points, N is the total number of data points and M is the number of parameters optimized in the model fit. In the fitting analysis of rather small micelles formed at $x = 0.25$ and 0.50 , we have used six fitting parameters (a , b , c , ϱ , ϕ_{mic} , and z_{eff}), in addition to the scaling parameter $a_1 = n(\Delta\rho_{core}V_{core})^2$ and residual background scattering, where ϕ_{mic} is the volume fraction of micelles and z_{eff} denotes the effective overall charge of the micelles. The latter two parameters were, however, seen to have little influence on the scattering behavior and could not be accurately determined from the model fitting analysis due to the high ionic strengths in the solutions (fixed to $[\text{NaCl}] = 154 \text{ mM}$). The micelles formed at $x = 0.75$ were too large to determine their size from the SAXS data which were fitted using three parameters (a , b , and ϱ). The shell thickness d was fixed to 10 \AA for all samples.

Contrast profile of three described in Table.1

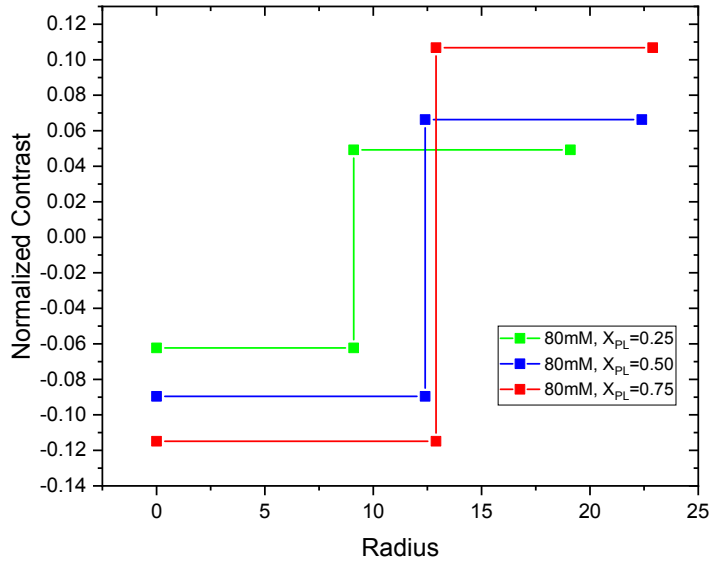


Figure S1: X-ray contrast profile between the core and shell of mixed NaDC-DMPC micelles at different compositions X_{PL} and fixed total concentration $[NaDC] + [DMPC] = 80 \text{ mM}$. The fitted SAXS curve has been shown in the article Fig.4.

The excess scattering length density of the core-and-shell has been normalized by the scattering length density of water. The radius that has been shown in the Fig.S1 is the minor axis of ellipsoidal micelles.

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