Supporting Information

Structural Analysis of Hydrophobe-Uptake Micelle of an Amphiphilic Alternating Copolymer in Aqueous Solution

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Ellipsoidal Flower Micelle Model

Here, we consider the ellipsoidal flower micelle schematically shown in Figure S1 as a possible model for the hydrophobe-uptake micelle, and compare it with the experimental results of light scattering and SAXS presented in the text.

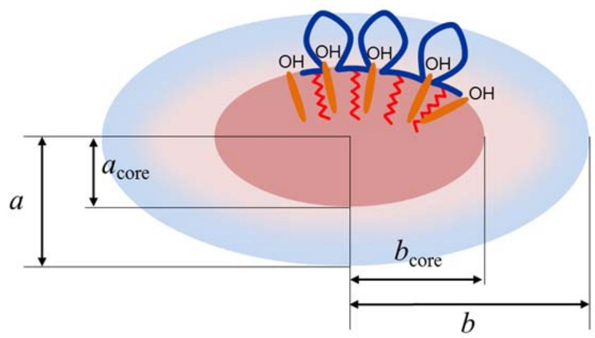

Figure S1. Ellipsoidal flower micelle model for the hydrophobe-uptake polymer micelle.

In Figure S1, a_{core} and b_{core} are the equatorial and polar radii of the hydrophobic core, and a and b are the equatorial and polar radii of the whole micelle. Because the flower micelle has loop chains with the height d_{loop} outside the hydrophobic core, a and b are related to a_{core} and b_{core} by

$$a = a_{\text{core}} + d_{\text{loop}}, \quad b = b_{\text{core}} + d_{\text{loop}} \tag{S1}$$

The volume V_{core} and the interfacial area A_{core} of the hydrophobic core are given by

$$V_{\mathrm{core}} = \frac{4\pi}{3} a_{\mathrm{core}}^2 b_{\mathrm{core}} \tag{S2}$$

and

$$A_{\mathrm{core}} = 2\pi \left(a_{\mathrm{core}}^2 + \frac{a_{\mathrm{core}} b_{\mathrm{core}} \sin^{-1} e_{\mathrm{core}}}{e_{\mathrm{core}}} \right) \tag{S3}$$

with the eccentricity e_{core} defined by

$$e_{\mathrm{core}} = \sqrt{1 - \left(a_{\mathrm{core}} / b_{\mathrm{core}} \right)^2} \tag{S4}$$

In eq S3, we have assumed the prolate for the ellipsoidal micelle.

The hydrophobic core consists of dodecyl groups belonging to P(MAL/C12) chains and DOH. According to eq 13, we can calculate V_{core} by

$$V_{\mathrm{core}} = \frac{4\pi}{3} a_{\mathrm{core}}^2 b_{\mathrm{core}} = \lambda \upsilon_{\mathrm{C12}} \left(\frac{N_{\mathrm{u}} h}{l_{\mathrm{loop}}} + m_{\mathrm{R}} \right) + \frac{m_{\mathrm{R}} M_{\mathrm{w,1}}}{M_{\mathrm{H}}} \frac{c_{\mathrm{H}}}{c_{\mathrm{P}}} \upsilon_{\mathrm{H}} \tag{S5}$$

The hydrodynamic radius R_{H} of the prolate micelle is calculated by[1]

$$R_{\mathrm{H}} = \frac{eb}{\ln(1+e) - \ln(a/b)} \tag{S6}$$

with the eccentricity e defined by

$$e = \sqrt{1 - (a/b)^2} \tag{S7}$$

We can determine a_{core} and b_{core} as well as a and b (cf. eq S1) from eqs S5 and S6 using the experimental values of V_{core} and R_{H}. The results are listed in Table S1, where we have assumed $\lambda = 1.0$. The maximum value of a_{core} in Table S1 agrees with the contour length of the dodecyl group,[2] being consistent with the *cosurfactant* model for DOH. We can determine similarly a_{core} and b_{core} when the ellipsoidal micelle is oblate from the experimental results of V_{core} and R_{H}. The results of a_{core} and b_{core} provide a much larger A_{core} than that calculated for the prolate by eq S3. Thus, the oblate is unfavorable in comparison with the prolate.

Table S1. Parameters of the prolate flower micelle.

$c_{\mathrm{H}}/c_{\mathrm{R}}$	m_{R} [a]	R_{H}/nm [a]	a_{core}/nm	b_{core}/nm	a/nm	b/nm
0	1.3	3.0	1.1	1.1	3.0	3.0
0.1	2.2	4.1	1.3	4.3	3.2	6.1
0.2	2.4	4.8	1.4	6.3	3.3	8.2
0.3	4.1	6.3	1.7	11	3.5	13

[a] Taken from Table 1 in the text.

The particle scattering function $P_{\text{flower}}(k)$ of the prolate flower micelle may be approximated to that of a concentric prolate where the inner and outer prolates correspond to the hydrophobic core and loop chains region, respectively. Taking the dispersity of the hydrophobic core size into account, we can write $P_{\text{flower}}(k)$ as[3]

$$P_{\text{flower}}(k) = \frac{1}{\sqrt{\pi}} \int P_{\text{prolate}}(k; a''_{\text{core}})^2 \exp(-x^2) \mathrm{d}x \tag{S8}$$

Here,

$$P_{\text{prolate}}(k; a''_{\text{core}}) = \left[\frac{\Delta\tilde{\rho}_{\text{c}} a''^{\,3}_{\text{core}} f_{\text{core}} \Psi^{1/2}(ka''_{\text{core}}; f_{\text{core}}) + a^3 f \Psi^{1/2}(ka; f)}{\Delta\tilde{\rho}_{\text{c}} a''^{\,3}_{\text{core}} f_{\text{core}} + a^3 f} \right]^2 \tag{S9}$$

with

$$a''_{\text{core}} \equiv \sqrt{2}\sigma_{\text{core}} x + a_{\text{core}}, \quad f_{\text{core}} = \frac{b_{\text{core}}}{a_{\text{core}}}, \quad f = \frac{b}{a} \tag{S10}$$

$$\Psi(ka'; f') = \frac{9}{2}\sqrt{\pi} \sum_{l=0}^{\infty} \sum_{m=0}^{l} \frac{(-1)^{l+m} \exp(-d_{lm})}{(l+2)(l+3)(2m+1)} (ka')^{2l} (1-f'^2)^m \tag{S11}$$

and

$$d_{lm} = \ln\Gamma\left(l + \frac{5}{2}\right) + \ln\Gamma(l-m+1) + \ln\Gamma(m+1) \tag{S12}$$

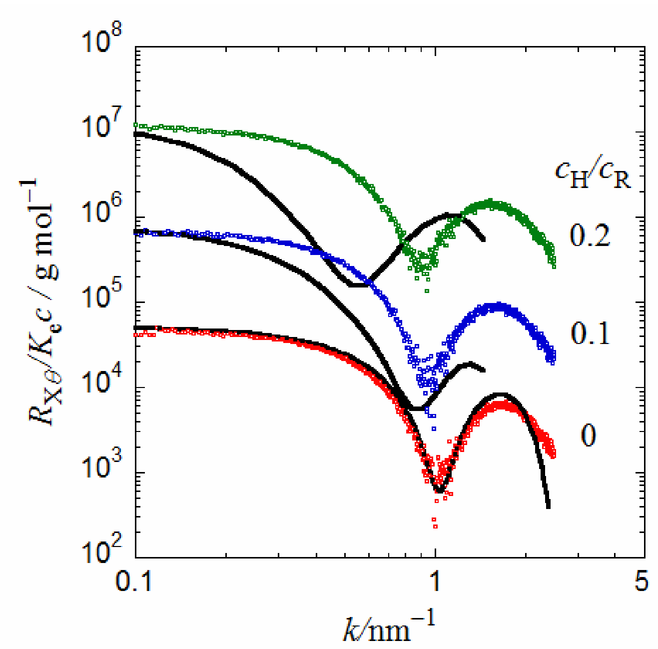

Figure S2. Comparison of the SAXS profiles with the prolate flower micelle model; σ_{core} = 0.13 and 0.090 for $c_{\text{H}}/c_{\text{R}}$ = 0.1 and 0.2, respectively. The data points and the theoretical curves for $c_{\text{H}}/c_{\text{R}}$ = 0.1 and 0.2 are shifted vertically for viewing clarity.

where $\Gamma(n)$ is the Gamma function. The scattering function $R_{X\theta}/K_e c$ is calculated by

$$\frac{R_{X\theta}}{K_e c} = \frac{M_w P_{\text{flower}}(k)}{1 + 2A_2 M_w P_{\text{flower}}(k)c} \tag{S13}$$

The theoretical results for c_H/c_R = 0.1 and 0.2 calculated by eqs 8-13 with the parameters a_{core}, b_{core}, a, and b listed in Table S1 are shown in Figure S2 by solid curves. (It was difficult to calculate the scattering function for c_H/c_R = 0.3 because of ill convergence of the series expansion in eq S11.) The theoretical curves for c_H/c_R = 0.1 and 0.2 provide minima at k appreciably smaller than the experimental results. Similarly, we calculated the scattering function of the oblate flower micelle of which a_{core}, b_{core}, a, and b were determined from eqs S5 and S6 using the experimental values of V_{core} and R_H. The results did not fit the experimental scattering functions for c_H/c_R = 0.1 and 0.2. Therefore, both prolate and oblate flower micelle models cannot fit to the R_H and SAXS data consistently. From the better fittings shown in Figures 6b and 7b in the text, we conclude that the DOH-uptake micelle of P(MAL/C12) does not have a single prolate hydrophobic core but multiple spherical hydrophobic cores.

The SAXS profiles in Figure S2 may be fitted to eqs S8-S13, if one chooses different set of parameters arbitrarily. Thus, it is not enough to check the hydrophobe-uptake micelle model only by the SAXS result, because of many fitting parameters, and it is very important to compare the model by different experimental techniques. It is noted that there are no free parameters to adjust in Figure S2.

References

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