How Viscoelastic Solution of Wormlike Micelles Transforms into Microemulsion upon Absorption of Hydrocarbon: A New Insight

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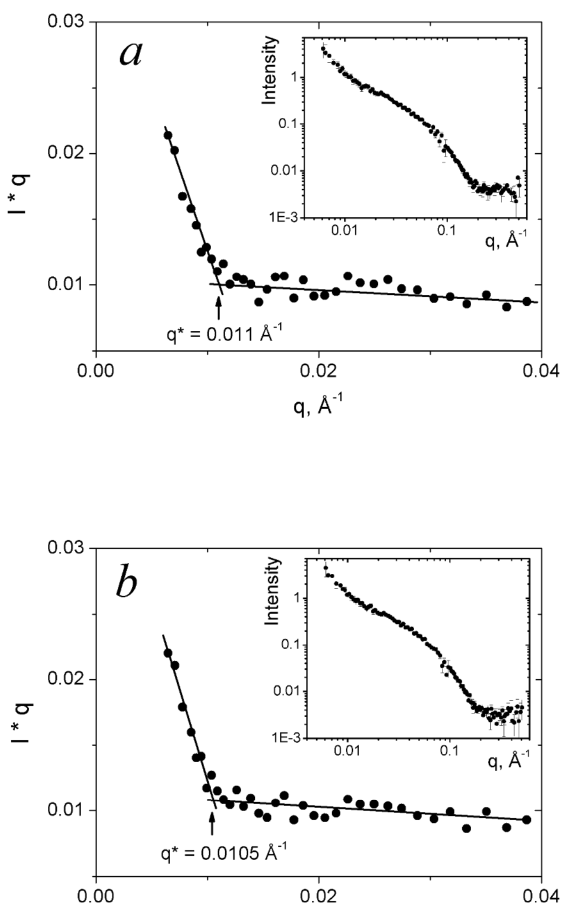
SUPPORTING INFORMATION

Determination of persistence length of cylindrical micelles l_p from SANS data. To investigate how solubilized hydrocarbon affects the persistence length of the micelles, we diluted 3 wt.% potassium oleate solutions containing different amounts of added *n*-dodecane (0, 0.02, 0.05 and 0.09 wt.%) with 6 wt.% KCl in D_2O in order to get the final surfactant concentration of 0.11 wt.%. It has been previously shown [V. S. Molchanov, O. E. Philippova, A. R. Khokhlov, Y. A. Kovalev and A. I. Kuklin, *Langmuir*, 2007, **23**, 105] that in 0.11 wt.% aqueous solutions potassium oleate forms short cylindrical micelles, which are near the overlap threshold. At these conditions interactions between the micelles are negligible, what allows to determine persistence length from the low-q part of the scattering curves. The results of SANS measurements are shown in Fig. S1. Persistence length was determined from the Holtzer plot (dependence of the intensity times the scattering vector ($I*q$) on q) as $l_p = 1.9 / q*$, where $q*$ is the scattering vector below which an upturn of $I*q$ is seen [C. A. Dreiss, *Soft Matter*, 2007, **3**, 956; G. Jerke, J. S. Pedersen, S. U. Egelhaaf, P. Schurtenberger, *Langmuir*, 1998, **14**, 6013]. Table 1 of the main text shows the l_p values thus obtained at different hydrocarbon concentrations.



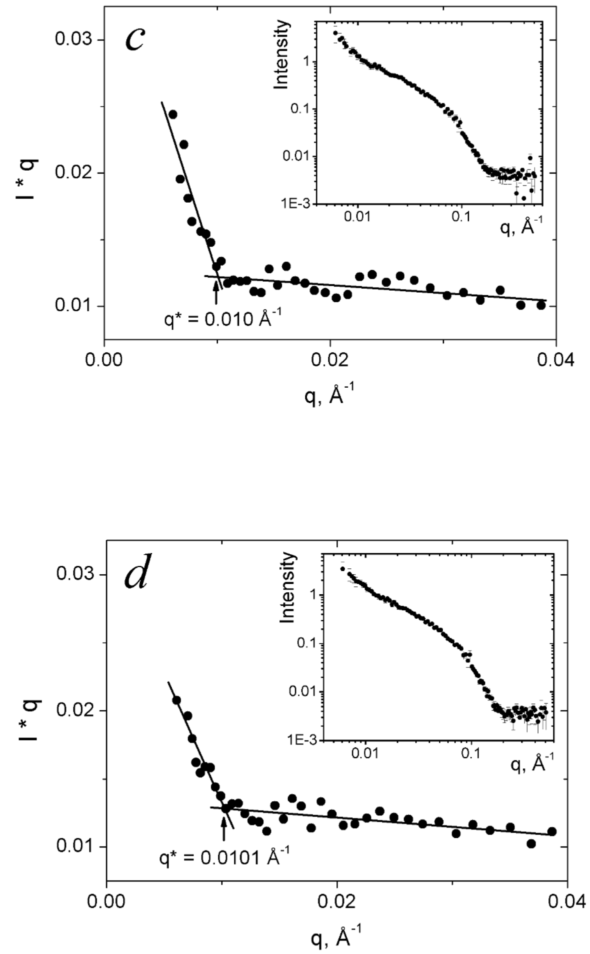


Figure S1. Dependences of $I*q$ on q (Holtzer plots) and scattering profiles (insets) for 0.11 wt. % potassium oleate solutions in the presence of different concentrations of *n*-dodecane: 0 wt.% (a), 0.00073 wt.% (b), 0.00183 wt.% (c), 0.0033 wt.% (d). Temperature: 20^{0}C. Solvent: 6 wt.% KCl in D_2O.

Theoretical estimation of the scission energy of a cylindrical micelle with solubilized hydrocarbon. We propose a very simple model which semi-quantitatively estimates the reduction of the scission energy of cylidrical micelles upon addition of hydrocarbons.

Let us consider first a single end-cap of a cylindrical micelle, and assume that hydrocarbon forms a core of semi-spherical shape of radius r inside it. Then, the maximal radius of end-cap becomes $b_{max} + r$ instead of b_{max} in the absence of hydrocarbon, while the volume per hydrophobic tail of an amphiphile molecule is now

$$v = \frac{a_{sph}\left(b_{\max}+r\right)}{3} - \frac{a_{sph}\left(b_{\max}+r\right)}{3}\frac{r^3}{\left(b_{\max}+r\right)^3} \qquad \text{(S1)}$$

where a_{sph} is the area per molecule, and the second term corresponds to the volume occupied by hydrocarbons. The surface area per molecule is therefore given by

$$a_{sph}\left(r\right) = \frac{3v\left(b_{\max}+r\right)^2}{\left(b_{\max}+r\right)^3 - r^3} = a_{sph}^0 \frac{1+2\xi+\xi^2}{1+3\xi+3\xi^2} < a_{sph}^0 \qquad \text{(S2)}$$

where we introduced $\xi = r/b_{\max}$ and $a^0_{\mathrm{sph}} = 3v/b_{\max}$, the latter being a surface area per molecule in an end-cap without hydrocarbon droplet inside. As is seen from eq. S2, the surface area a_{sph} is a decreasing function of r. Now, the end-cap energy $\delta(r)$ is given by (compare with equation 7)

$$\delta\left(r\right) \approx 4\pi\gamma\left(b_{\max}+r\right)^2\left(1-\frac{a_0}{a_{sph}\left(r\right)}\right)^2 = \delta_0\left(\frac{1+2\xi+\xi^2-\beta\left(1+3\xi+3\xi^2\right)}{\left(1-\beta\right)\left(1+\xi\right)}\right)^2 \qquad \text{(S3)}$$

where $\delta_0 = \delta\ (r = 0)$ is given by equation (7) and we introduce a new variable $\beta = a_{sph}^0/a_0;\quad 2/3 \le \beta < 1$ (see the comment after eq. 3). Note that there exists a value of $\xi = \xi_0$, at which the scission energy $\delta(r_0)$ equals zero. This critical value of ξ is given by the solution of the equation

$$\beta = \left(1+2\xi_0+\xi_0^2\right)\big/\left(1+3\xi_0+3\xi_0^2\right);\quad \xi_0 = \frac{2-3\beta+\sqrt{\beta\left(4-3\beta\right)}}{2\left(3\beta-1\right)};\quad 0<\xi_0<\frac{1}{\sqrt{3}}. \qquad \text{(S4)}$$

The end-caps with droplets of the size $r_0 = \xi_0 b_{\max}$ inside are thus not disadvantageous at all compared to the linear parts of the micelles. Therefore, if there is enough hydrocarbon in the solution to form such droplets, the cylindrical micelles will split more and more, until only spherical layers of amphiphilic molecules with hydrocarbon droplets inside (microemulsion droplets) will remain in the solution. Note that since the value of β does not exceed 2/3, the corresponding value of $r_0 < b_{max}/\sqrt{3}$, and therefore the critical concentration of hydrocarbon at which the transition from cylindrical micelles to microemulsion droplets takes place can be estimated as

$$c_h^{crit} = \frac{c}{\left(1+\xi_0^{-1}\right)^3 - 1} \leq \frac{c}{\left[\left(1+\sqrt{3}\right)^3 - 1\right]} \approx c/19. \qquad \text{(S5)}$$