Electronic Supplementary Material (ESI) for Soft Matter

Self-assembly of onions induced by charge and rheological properties in anionic/nonionic surfactant solutions

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Supporting Information

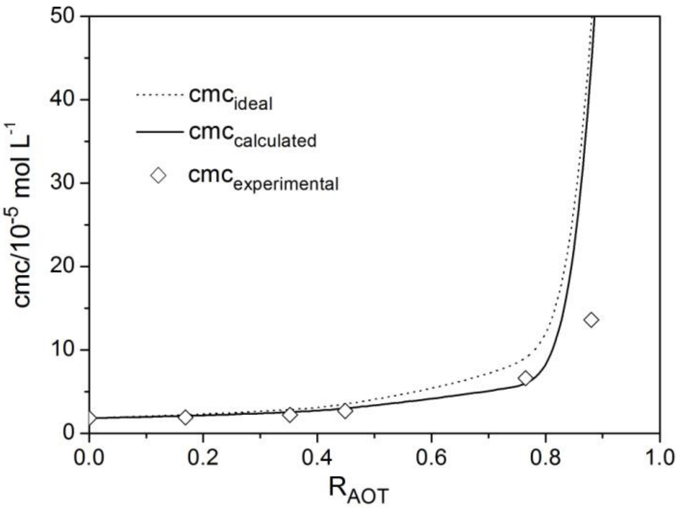

Fig. S1 Plots of the mixed cmc versus the surfactant composition R_{AOT}. Symbols represent the measured values, the dashed line represents the ideal results with $\beta = 0$, and the solid line refers to the calculated case with $\beta^m = -1.88$.

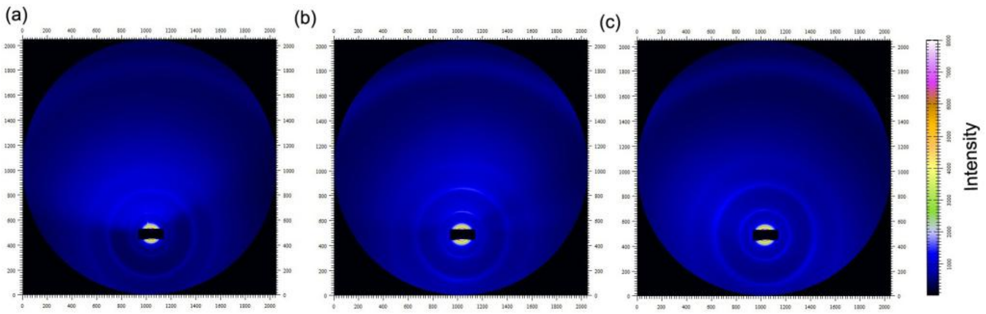

Fig. S2 The two dimensional SAXS scattering patterns of the lamellar structure with R_{AOT} = 0.4 at three different surfactant concentrations at 25.0 ± 0.1°C: (a) 15, (b) 18, and (c) 25 wt%.

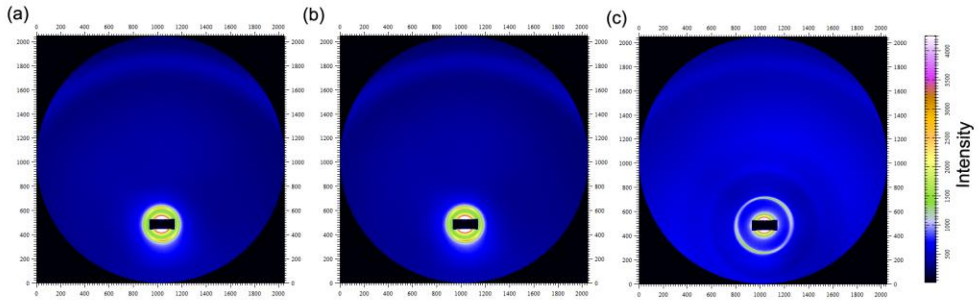

Fig. S3 The two dimensional SAXS scattering patterns of the lamellar structure with R_{AOT} = 0.8 at three different surfactant concentrations at 25.0 ± 0.1°C: (a) 15, (b) 18, and (c) 25 wt%.

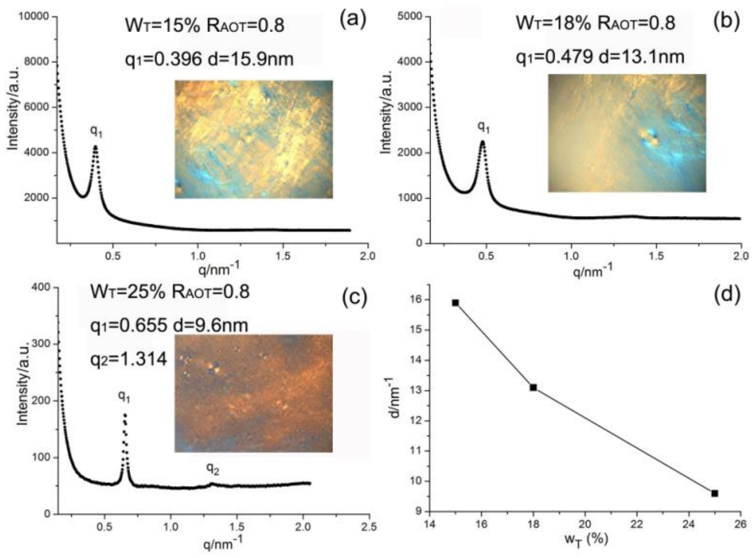

Fig. S4 Small angle x-ray scattering curves of the lamellar structures with R_{AOT} = 0.8 at three different surfactant concentrations: (a) 15%, (b) 18%, and (c) 25%. (d) Plot of the interlamellar distance versus the whole concentration. Insets are the polarized images of the lamellar phase samples.

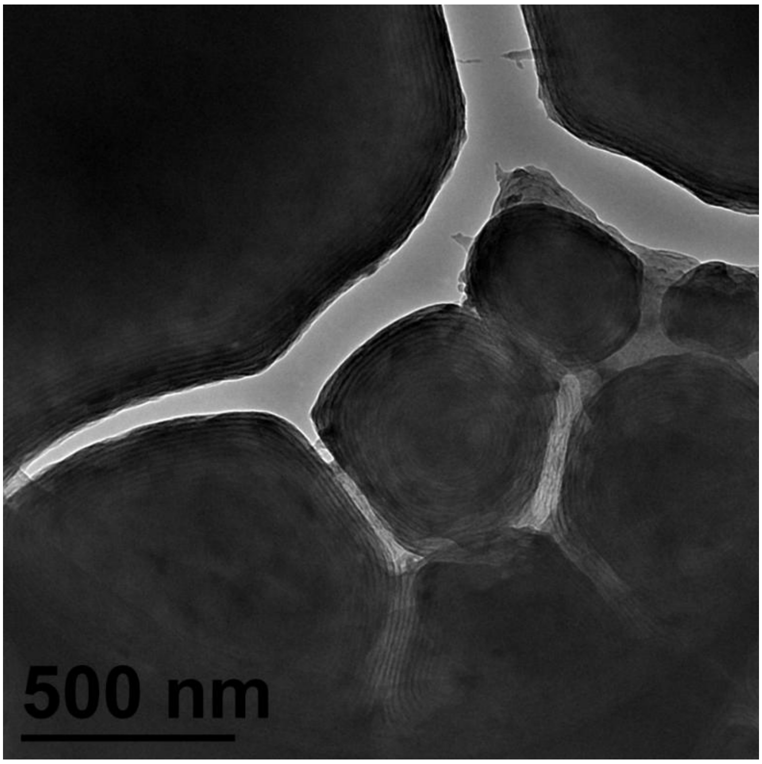

Fig. S5 Cryo-TEM images of lamellar phase solution with R_{AOT} = 0.4 at W_T=15%.

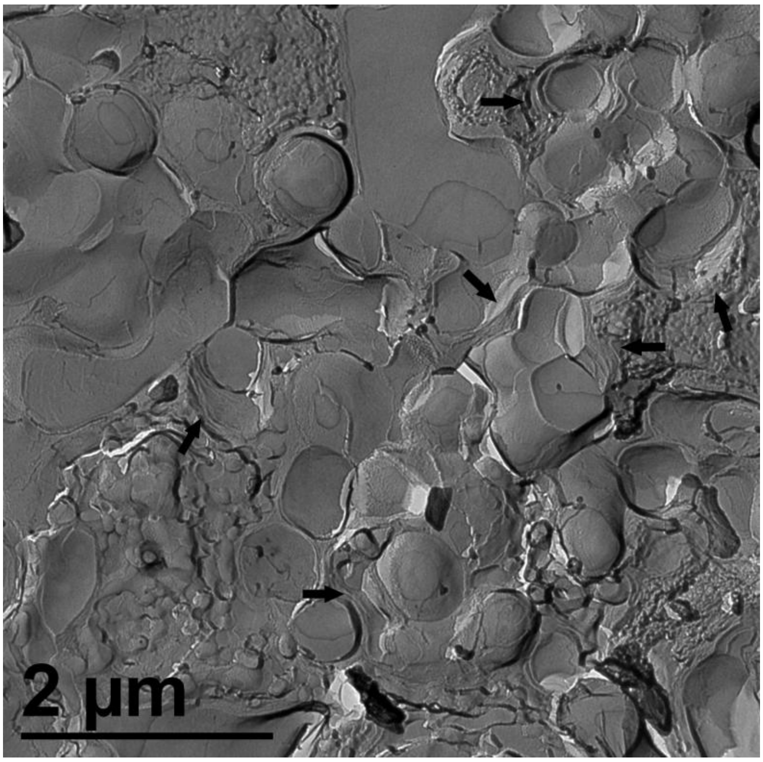

Fig. S6 FF-TEM images of lamellar phase solutions, W_T=15%, R_{AOT} = 0.8. Arrows show the multilamellar structures.

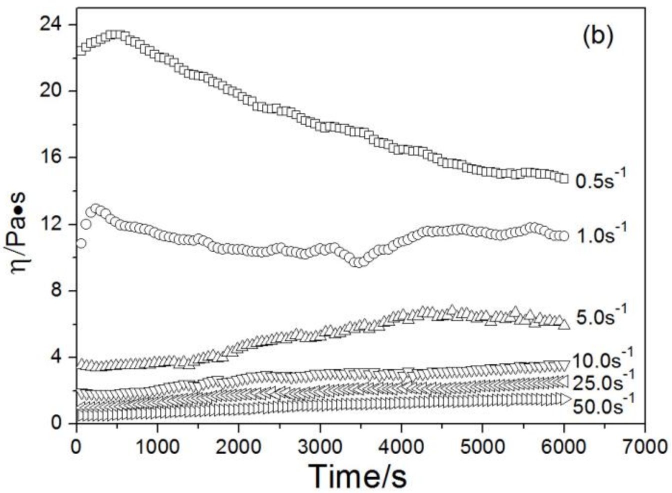

Fig. S7 Time evolution of shear viscosity for different shear rates in the different lamellar solutions at 25.0 ± 0.1°C. W_T=15%, R_{AOT} = 0.8.

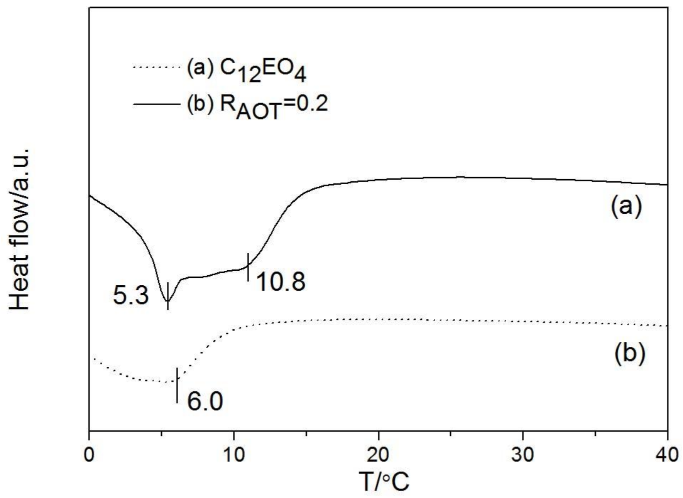

Fig. S8 DSC curves of lamellar phase samples at R_{AOT} = 0.0 (a) and 0.2 (b) where the total surfactant concentration is 25%.

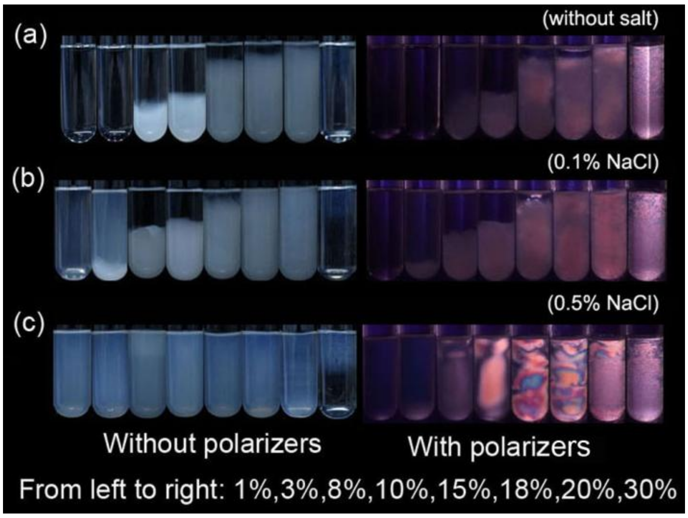

Fig. S9 Phase transition of AOT/$C_{12}EO_4$ aqueous solution with R_{AOT} = 0.5 induced by adding amount of NaCl at 25.0 ± 0.1°C. (a) Without salt, (b) 0.1% NaCl, and (c) 0.5% NaCl. From left to right, the surfactant concentration increases in the sequence of 1%, 3%, 8%, 10%, 15%, 18%, 20%, and 30%.

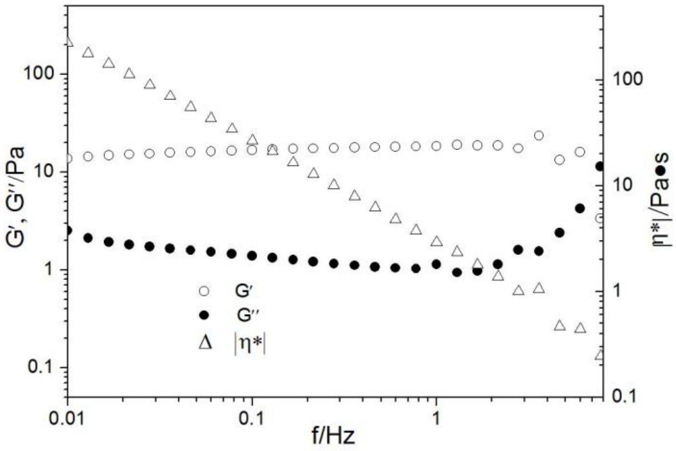

Fig. S10 Oscillatory rheogram for 15% L_1/L_α-phase solution with $R_{AOT} = 0.5$ after addition of 0.5% NaCl.

Annex. 1 Modeling of Mixed micellization

According to Rubingh's regular solution theory for mixed micelles,[1] the mixed cmc of AOT and $C_{12}EO_4$ system can be derived by Eq. (S1),

$$\frac{1}{cmc_{mix}} = \frac{\alpha}{f_1 cmc_1} + \frac{1-\alpha}{f_2 cmc_2} \tag{S1}$$

where α is the total molar fraction of AOT in the whole system; cmc_1 and cmc_2 are the cmc's of AOT and $C_{12}EO_4$ surfactants, respectively; f_1 and f_2 are the activity coefficients of AOT and $C_{12}EO_4$ in the mixed micelle.

In the case of ideal mixing, there is no net interaction, $f_1=f_2=1$ and the theoretical cmc can be calculated by Eq. (S2),[2]

$$\frac{1}{cmc_{mix}} = \frac{\alpha}{cmc_{AOT}} + \frac{1-\alpha}{cmc_{C12EO4}} \tag{S2}$$

The activity coefficients f_1 and f_2 are given by Eq. (S3),

$$f_1 = \exp[\beta(1-x_{AOT})^2] \qquad f_2 = \exp[\beta x_{AOT}^2] \tag{S3}$$

where x_{AOT} is the mole fraction of AOT in the mixed micelle. The magnitude of the interaction between the two surfactants can be expressed by single parameter β. When there is no net interaction, β=0. A negative β interaction parameter usually implies an attractive interaction and indicates a synergism in the mixing behavior. The interaction parameter β can be calculated by the following equations,

$$\frac{x_{AOT}^2 \ln\left(\frac{cmc_{mix}\alpha}{cmc_1 x_{AOT}}\right)}{(1-x_{AOT})^2 \ln\left(\frac{cmc_{mix}(1-\alpha)}{cmc_2(1-x_{AOT})}\right)} = 1 \tag{S4}$$

$$\beta = \frac{\ln\left(\frac{cmc_{mix}\alpha}{cmc_{AOT} x_{AOT}}\right)}{(1-x_{AOT})^2} \tag{S5}$$

References

1. D. N. Rubingh in "Solution Chemistry of surfactants" K. L. Mittal Ed. Vol 1, New York, 1979.
2. J. H. Clint, *J. Chem. Soc., Faraday Trans.*, 1975, **73**, 1327.