

Electronic Supplementary Information for

Spontaneous Vesicle Phase Formation by Pseudogemini Surfactants in Aqueous Solutions

Nan Sun,^a Lijuan Shi,^b Fei Lu,^a Shuting Xie,^a and Liqiang Zheng^{*a}

*^aKey Laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of
Education, Jinan 250100, China*

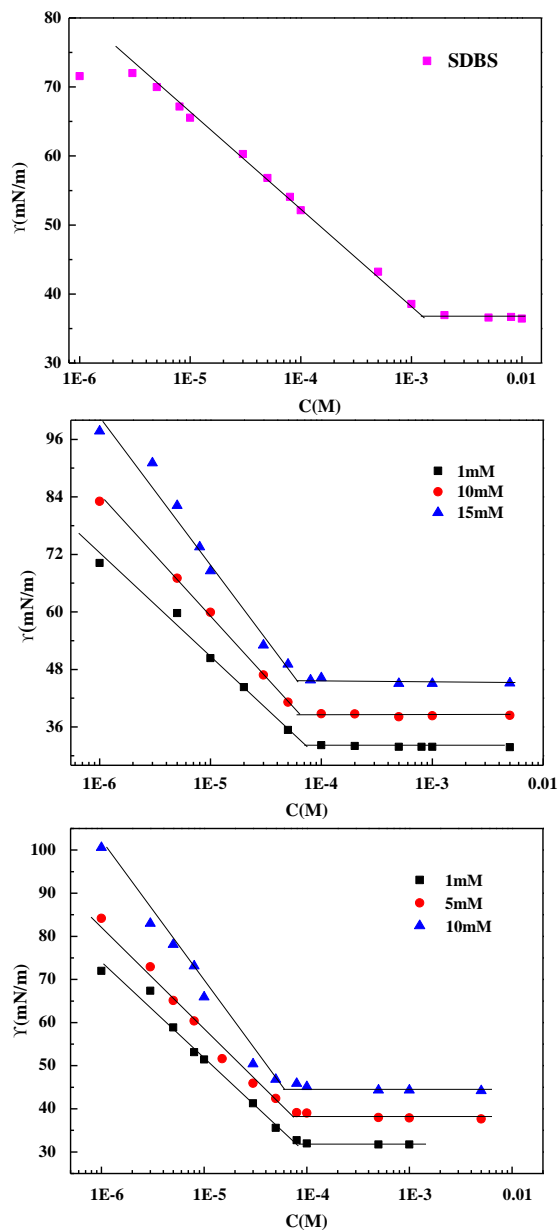
*^bKey Laboratory of Coal Science and Technology of Ministry of Education and Shanxi
Province, Taiyuan University of Technology, Taiyuan 030024, China*

Experimental details

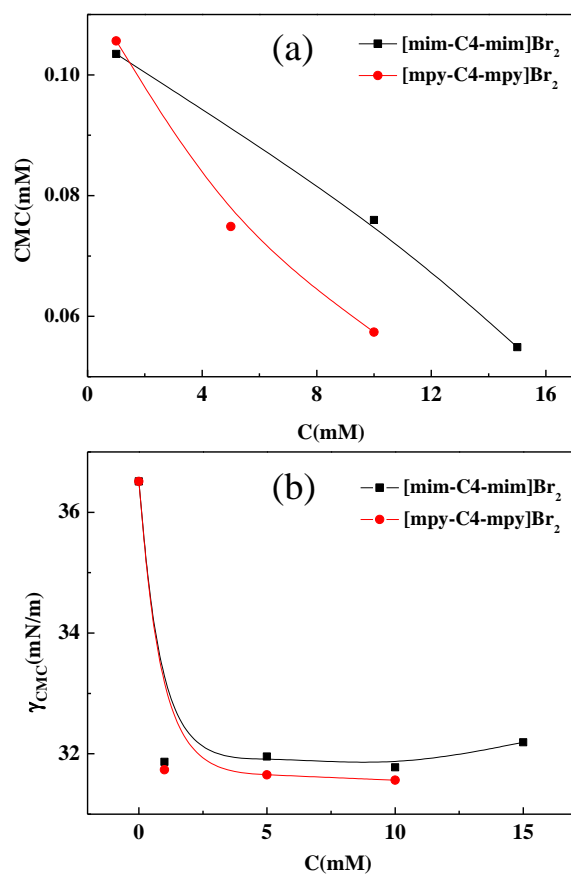
Surface tension measurements: The surface tension measurements were carried out on a Model JYW-200B tensiometer (Chengde Dahua Instrument Co., Ltd., accuracy ± 0.1 mN/m) using the ring method. Temperature was controlled $25 \pm 0.1^\circ\text{C}$ using a thermostatic bath. Each sample was equilibrated for 15 min under the test temperature to reach equilibrium before the measurement.

Dynamic Light Scattering: The droplet size distributions of the micelles and the vesicle phase were determined by dynamic light scattering (DLS, DynaPro NanoStar, Wyatt Instrument Co.) with an argon-ion laser operating at 658 nm. All measurements were made at the scattering angle of 90° . The temperature was controlled at 25°C with a thermostat (F31C, Julabo) with an accuracy of $\pm 0.1^\circ\text{C}$.

Additional results



FigureS1 Surface tension curves of SDBS plotted against the surfactant concentrations (C) at different salt concentrations: (a) without salt, (b) [mim-C₄-mim]Br₂, and (c) [mpy-C₄-mpy]Br₂. Surface tension curves of salt concentrations above 1 mM are drawn by shifting the surface tension values appropriately.



FigureS2 Plots of the CMC (a) and γ_{CMC} (b) values of SDBS against the concentrations of added salt.

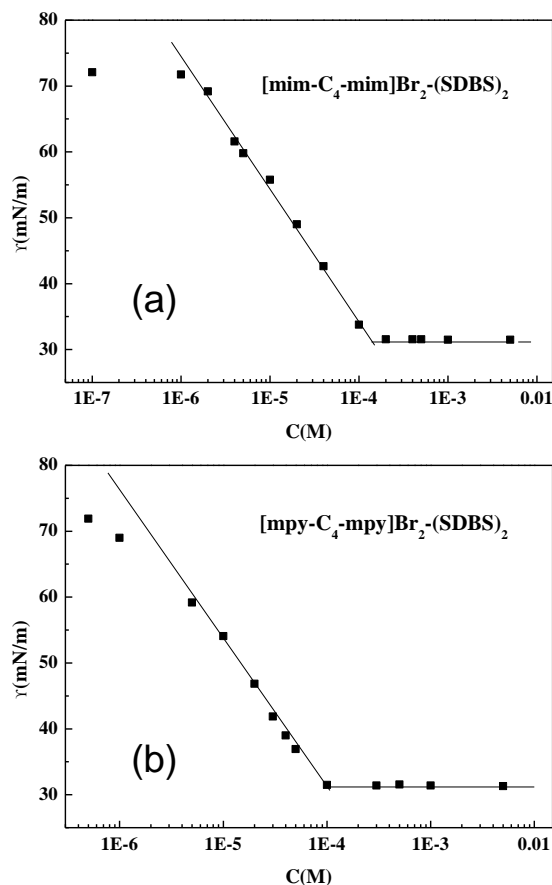


Figure S3. Surface tension curves of $[\text{mim-C}_4\text{-mim}]\text{Br}_2\text{-(SDBS)}_2$ (a)

$[\text{mpy-C}_4\text{-mpy}]\text{Br}_2\text{-(SDBS)}_2$ (b) plotted against the surfactant concentrations (C) at 25°C .

Figure S3 shows the variation of surface tension against pseudogemini surfactant concentrations at 25°C . The surface tension decreases with increasing pseudogemini surfactant concentrations, and then reaches a clear break point which is taken as the critical micelles concentration (CMC). The amount of adsorbed surfactant (Γ) at the air-water interface can be calculated using the Gibbs adsorption isotherm:^[1]

$$\Gamma = -\frac{1}{nRT} \left(\frac{\partial \gamma}{\partial \ln C} \right)_T \quad (\text{mmol/m}^2) \quad [1]$$

where R is the gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), T is the absolute temperature (K), C is the surfactant concentration ($\text{mol}\cdot\text{L}^{-1}$), and $\partial\gamma/\partial \ln C$ refers to the slope below the CMC in the surface tension plots. The value of n that stands for the number of species at the interface was taken as 2 for $[\text{mim-C}_4\text{-mim}]\text{Br}_2\text{-(SDBS)}_2$ and $[\text{mpy-C}_4\text{-mpy}]\text{Br}_2\text{-(SDBS)}_2$. The minimum area occupied (A) by a surfactant molecule at the air-solution interface was obtained from the saturated adsorption as follows:

$$A_{\min} = \frac{1}{N_A \cdot \Gamma_{\max}} (\times 10^{23} \text{ \AA}^2) \quad [2]$$

where N is Avogadro's number ($6.022 \times 10^{23} \text{ mol}^{-1}$), and Γ_{\max} is the maximum surface excess concentration.

Table S1. Surface properties and micellization parameters of $[\text{mim-C}_4\text{-mim}]\text{Br}_2\text{-(SDBS)}_2$ and $[\text{mpy-C}_4\text{-mpy}]\text{Br}_2\text{-(SDBS)}_2$.

	CMC mM	γ_{CMC} mN/m	Γ_{\max} 10^{-3} mmol/m^2	A_{\min} \AA^2	P
$[\text{mim-C}_4\text{-mim}]\text{Br}_2\text{-(SDBS)}_2$	0.1446	31.2	2.05	80.94	0.56
$[\text{mpy-C}_4\text{-mpy}]\text{Br}_2\text{-(SDBS)}_2$	0.1005	31.2	1.95	85.22	0.53

The packing parameter P is an important factor to interpret the self-assembled structure for a particular amphiphile. P is determined as $P=v/al$ by Israelachvili et al,^[2] where v is the effective hydrophobic chain volume, a is the effective headgroup area of the surfactant molecules, and l is the surfactant alkyl chain length. Surfactants with P below 1/3 tend to form spherical micelles, while P values between 1/3 and 1/2 prefer to form cylindrical aggregates and P values between 1/2 and 1 prefer to form bilayers. Surfactants with even higher values of P ($P > 1$) favor the formation of reverse structures.

The hydrocarbon chain length l can be calculated from the following Tanforde equation^[2]:

$$l = 1.5 + 1.265N \quad [3]$$

Here N is the number of carbon atoms in one hydrocarbon chain. So, l is obtained to be 21.1075 Å. The effective volume of the hydrocarbon chains v has been calculated from the equation, and the value is 444.35 Å³.

$$v_l (\text{Å}^3) = 27.4 + 26.9N \quad [4]$$

For the pseudogemini surfactant, the area of headgroup at the air/water interface was detected from surface tension measurement (Figure S3) and the value is about 80.94 Å² for [mim-C₄-mim]Br₂-(SDBS)₂ and 85.22 Å² for [mpy-C₄-mpy]Br₂-(SDBS)₂ at 25°C (Table S1). Thus, the calculated P value is 0.56 for SDBS/[mim-C₄-mim]Br₂/H₂O system and 0.53 for SDBS/[mpy-C₄-mpy]Br₂/H₂O system, which is consistent with the formation of bilayer structure.

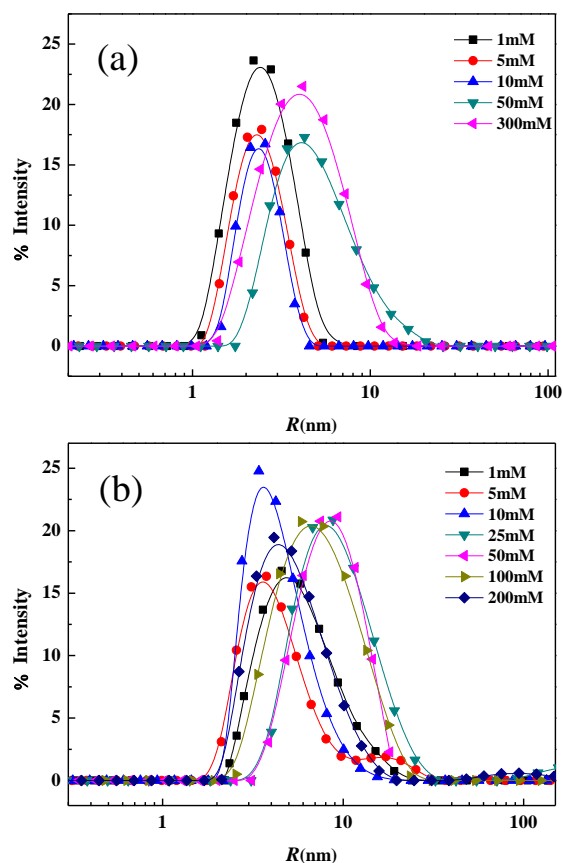


Figure S4. The size distribution of the [mim-C₄-mim]Br₂-(SDS)₂ (a) and [mpy-C₄-mpy]Br₂-(SDS)₂ (b) aggregates versus the logarithm of the [mim-C₄-mim]Br₂ or [mpy-C₄-mpy]Br₂ concentrations.

Dynamic light scattering (DLS) is utilized to further observe the aggregate size and morphology of the aqueous surfactant solution above the CMC value. The DLS results of [mim-C₄-mim]Br₂-(SDS)₂ system and [mpy-C₄-mpy]Br₂-(SDS)₂ system are shown in Figure S4, and the obtained hydrodynamic radii (R) of the aggregates from DLS are summarized in Table S2. Slightly variations of aggregates size are observed when the concentrations of [mim-C₄-mim]Br₂ or [mpy-C₄-mpy]Br₂ increase and only aggregates

with diameters lower than 20 nm formed. Therefore, we inferred that [mim-C₄-mim]Br₂-(SDS)₂ system and [mpy-C₄-mpy]Br₂-(SDS)₂ system did not experience a phase transition from micelles to vesicles with the increase of the concentrations of the mixed solutions.

Table S2. The obtained hydrodynamic radii (R) of [mim-C₄-mim]Br₂-(SDS)₂ and [mpy-C₄-mpy]Br₂-(SDS)₂ aggregates versus the [mim-C₄-mim]Br₂ or [mpy-C₄-mpy]Br₂ concentrations.

	R(nm)						
C _{[mim-C₄-mim]Br₂} (mM)	1	5	10	50	300	—	—
[mim-C ₄ -mim]Br ₂ -(SDBS) ₂	2.5	2.4	2.4	5.7	4.4	—	—
C _{[mpy-C₄-mpy]Br₂} (mM)	1	5	10	25	50	100	200
[mpy-C ₄ -mpy]Br ₂ -(SDBS) ₂	3.0	4.5	4.6	9.7	8.9	7.9	5.5

References

- 1 M. J. Rosen, A. W. Cohen, M. Dahanayake and X. Hua, *J. Phys. Chem.*, 1982, **86**, 541-545.
- 2 C. Tanford, *J. Phys. Chem.*, 1972, **76**, 3020-3024.