

## Supporting Information

### Complex Formation and Aggregate Transitions of Sodium Dodecylsulfate with An Oligomeric Connecting Molecule in Aqueous Solution

Linyi Zhu, Yuchun Han, Maozhang Tian, and Yilin Wang\*

Key Laboratory of Colloid and Interface Science, Beijing National Laboratory for  
Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190,  
P.R. China

#### 1. Confirmation of Lys-12-Lys Structure and Purity

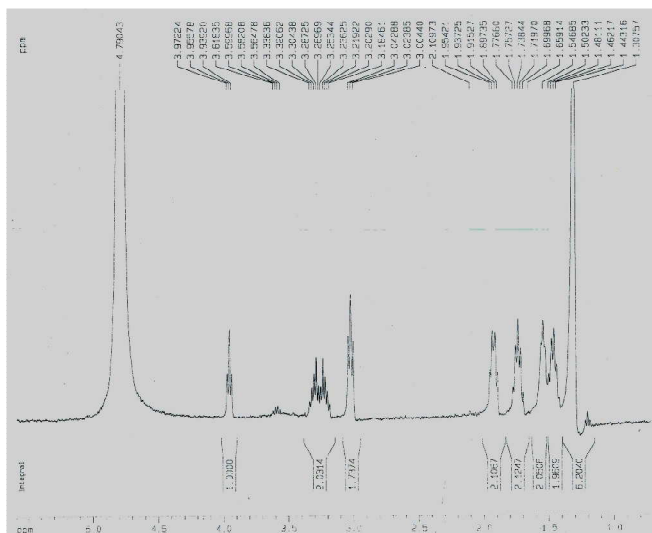


Figure S1 (a).  $^1\text{H}$  NMR of Lys-12-Lys.

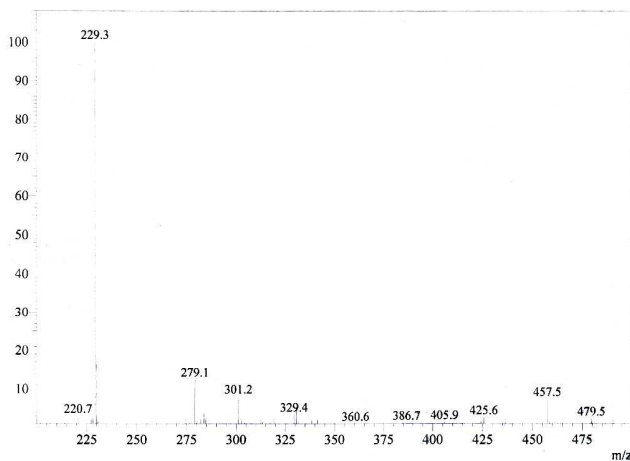
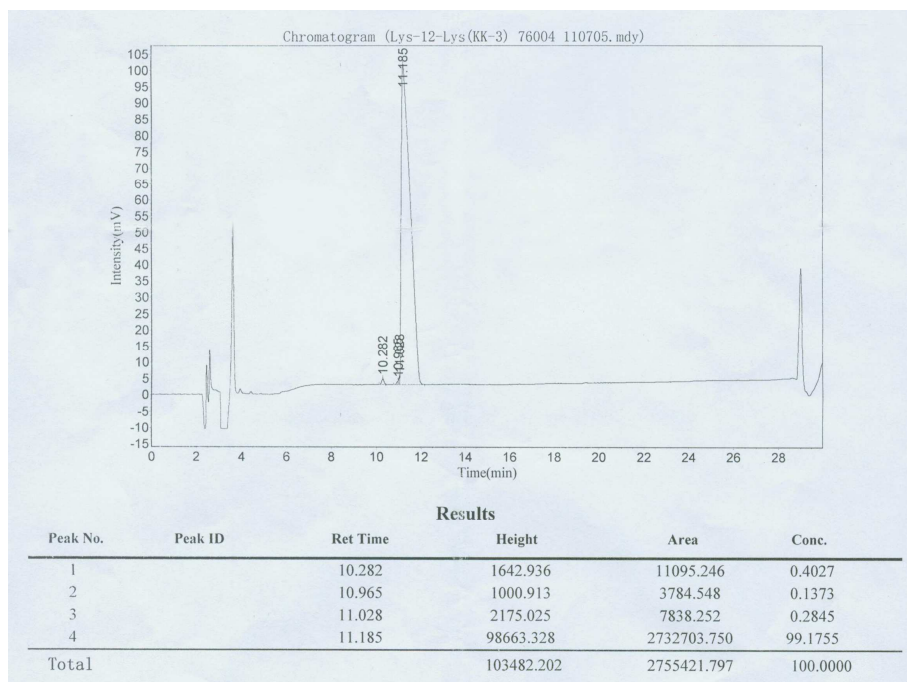
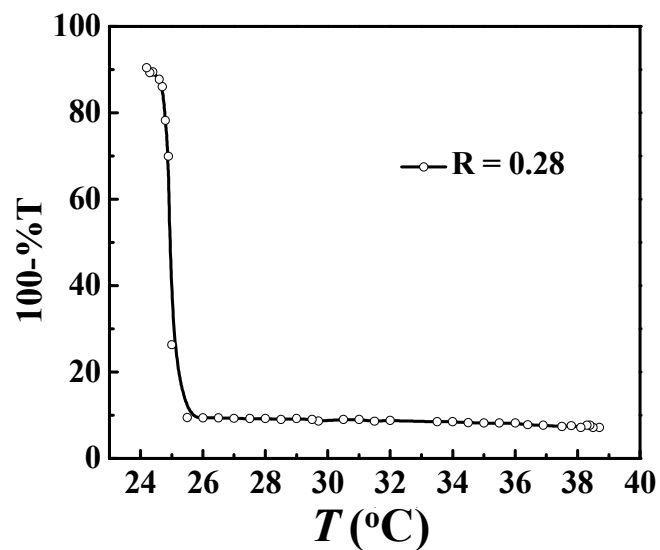


Figure S1 (b). Mass spectrum of Lys-12-Lys.



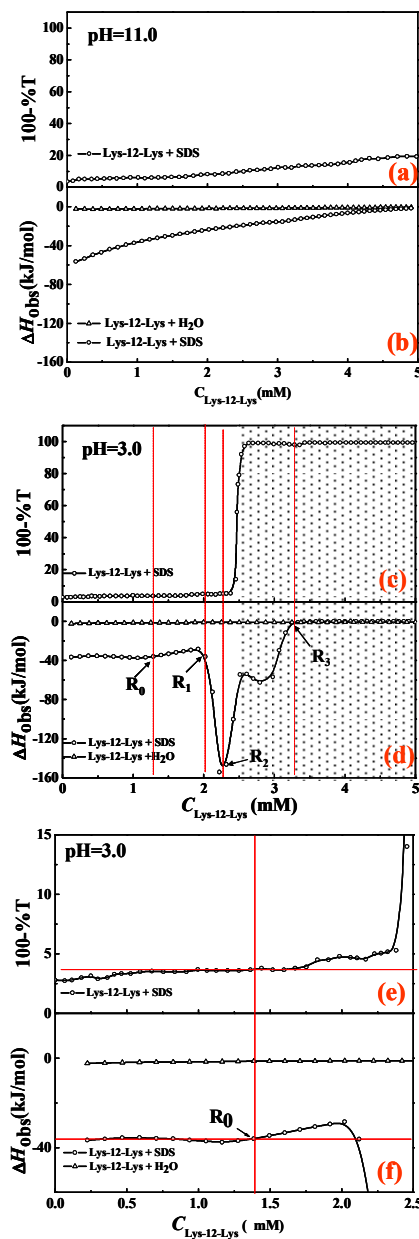
**Figure S1 (c).** High-performance liquid chromatography of Lys-12-Lys.

## 2. Temperature Dependence of the Mixed Solution of Lys-12-Lys and SDS



**Figure S2.** Dependence of the turbidity on temperature for the mixed solution of Lys-12-Lys and SDS at molar ratio 0.28 and pH 11.0.

### 3. Turbidity and ITC Results of Titrating Lys-12-Lys to SDS.



**Figure S3.** (a)(c) Turbidity curves for titrating Lys-12-Lys into 10 mM SDS solution at pH 11.0 and 3.0, and at  $34.0 \pm 0.1$  °C. (b)(d) ITC curves for titrating Lys-12-Lys into water and 10 mM SDS solution at pH 11.0 and 3.0, and at  $34.00 \pm 0.01$  °C. (e)(f) Enlarged plots of the turbidity and ITC curves in (c) and (d) for the Lys-12-Lys concentration lower than 2.5 mM. All the results are from the same experiment in Figure 3 as a function of the concentration of Lys-12-Lys.

#### 4. The Concentrations of Total and Unbound SDS for the Lys-12-Lys/SDS Solutions at Different Molar Ratios Estimated from ITC Curve

This calculation is a very approximate method. The total concentration of SDS was read from the x axis of Figure 8 (a). Assuming all the Lys-12-Lys molecules had been bound with SDS, the bound SDS concentration was approximately obtained by timing the concentration of Lys-12-Lys with the binding number. Then the concentration of the unbound SDS was calculated by subtracting the bound SDS concentration from the total SDS concentration.

**Table S1.** The Concentrations of Total ( $C_{\text{SDS}}$ ) and Unbound SDS ( $C_{\text{SDS-free}}$ ) for the Lys-12-Lys/SDS Solutions at Different Molar Ratios Estimated from ITC Curve.

R	vesicle&micelle <sup>a</sup>		vesicle <sup>b</sup>	
	$C_{\text{SDS}}$ (mM)	$C_{\text{SDS-free}}$ (mM)	$C_{\text{SDS}}$ (mM)	$C_{\text{SDS-free}}$ (mM)
0.15	3.97	0.40	0.76	0.08
0.20	5.00	~0.00	1.19	~0.00

<sup>a</sup> The concentrations at the second minimum values of ITC curves where vesicles are transforming to micelles. <sup>b</sup> The concentrations at the start point of the vesicle formation.

#### 5. ITC Analysis Process for Single Set of Identical Sites

In the following equations,

$K_b$  = binding constant;

$n$  = number of sites;

$\Theta$  = fraction of sites occupied by ligand (SDS);

$M_t$  and  $[M]$  are bulk and free concentration of Lys-12-Lys;

$X_t$  and  $[X]$  are bulk and free concentration of ligand SDS in  $V_0$ ;

$V_0$  = active cell volume;

$\Delta V_i$  = injection volume;

$Q$  = the heat content;

$Q_i$  = heat content from the completion of the  $i$ th injection.

The interaction process may be described in a simplified fashion using equation (1).



In the process, the binding constant and the concentration of the SDS can be expressed as

follows:

$$K_b = \frac{\Theta}{(1 - \Theta)[X]} \quad (2)$$

$$X_t = [X] + n\Theta M_t \quad (3)$$

Combining equations (2) and (3) above gives:

$$\Theta^2 - \Theta \left[ 1 + \frac{X_t}{nM_t} + \frac{1}{nK_b M_t} \right] + \frac{X_t}{nM_t} = 0 \quad (4)$$

The total heat content  $Q$  of the solution contained in  $V_0$  at fractional saturation  $\Theta$  is:

$$Q = n\Theta M_t \Delta H V_0 \quad (5)$$

Solving the quadratic equation (4) for  $\Theta$  and then substituting this into equation (5) gives:

$$Q = \frac{nM_t \Delta H V_0}{2} \left[ 1 + \frac{X_t}{nM_t} + \frac{1}{nK_b M_t} - \sqrt{\left( 1 + \frac{X_t}{nM_t} + \frac{1}{nK_b M_t} \right)^2 - \frac{4X_t}{nM_t}} \right] \quad (6)$$

So the calculated heat released in the  $i$ th injection,  $\Delta Q_{(i)}$  can be expressed as:

$$\Delta Q(i) = Q(i) + \frac{dV_t}{V_0} \left[ \frac{Q(i) + Q(i-1)}{2} \right] - Q(i-1) \quad (7)$$

In the experiments, we can determine the practical heat released in the  $i$ th injection. The process of fitting experimental data involves 1) initial guesses (which most often can be made accurately enough by Origin) of  $n$ ,  $K_b$ , and  $\Delta H$ ; 2) calculation of  $\Delta Q_{(i)}$  for each injection and comparison of these values with the measured heat for the corresponding experimental injection; 3) improvement in the initial values of  $n$ ,  $K_b$ , and  $\Delta H$  by standard Marquardt methods; 4) iteration of the above procedure until no further significant improvement in fit occurs with continued iteration. More information about the model analysis can be found in ITC Data Analysis in Origin® Tutorial Guide Version 7.0.