The Evolution of Self-assemblies in Mixed System of Oleic Acid/ Diethylenetriamine Based on the Transformation of Electrostatic Interactions and Hydrogen Bonds

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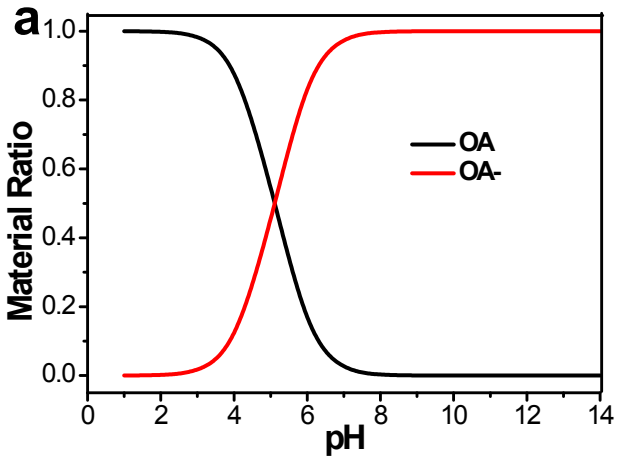
Supporting Information

1. The species distribution of oleic acid and diethylenetriamine.

The pKa value of the oleic acid is 5.1. And diethylenetriamine possesses three pKb values 3.98, 4.79 and 9.58. The species distribution of oleic acid and diethylenetriamine at the different pH value is all obtained by the eq as follow:

$$x_i = \frac{[H^+]^i \prod_{i=0}^{n-i} K_{a_i}}{\sum_{i=0}^{n} [H^+]^i \prod_{i=0}^{n-i} K_{a_i}} (K_{a_0} = 1; i = 0, 1 \ldots, \mathrm{n})$$



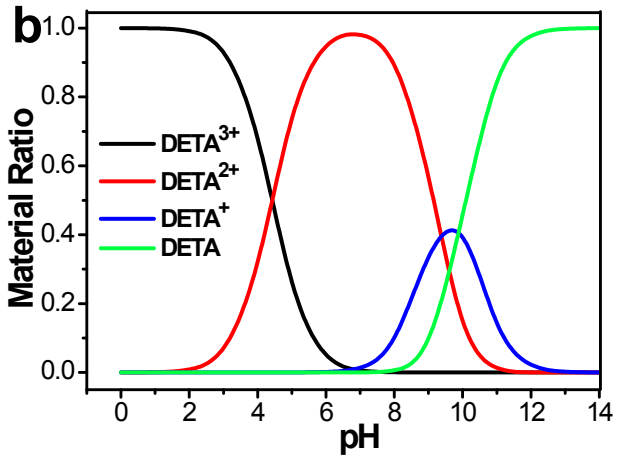


Figure S1 The species distribution of a) oleic acid solution and b) diethylenetriamine solution at 25 °C.

2. The DLS results.

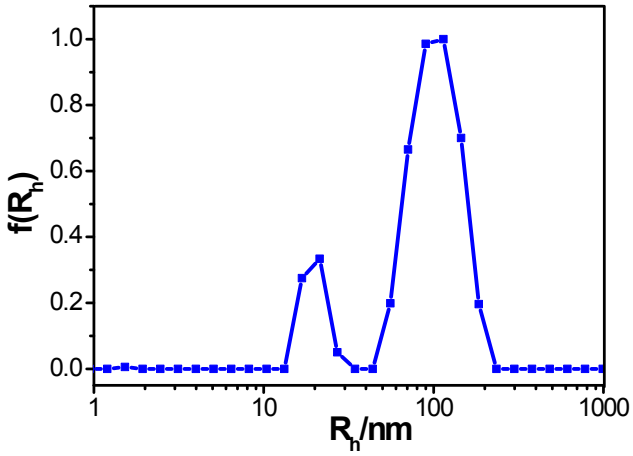
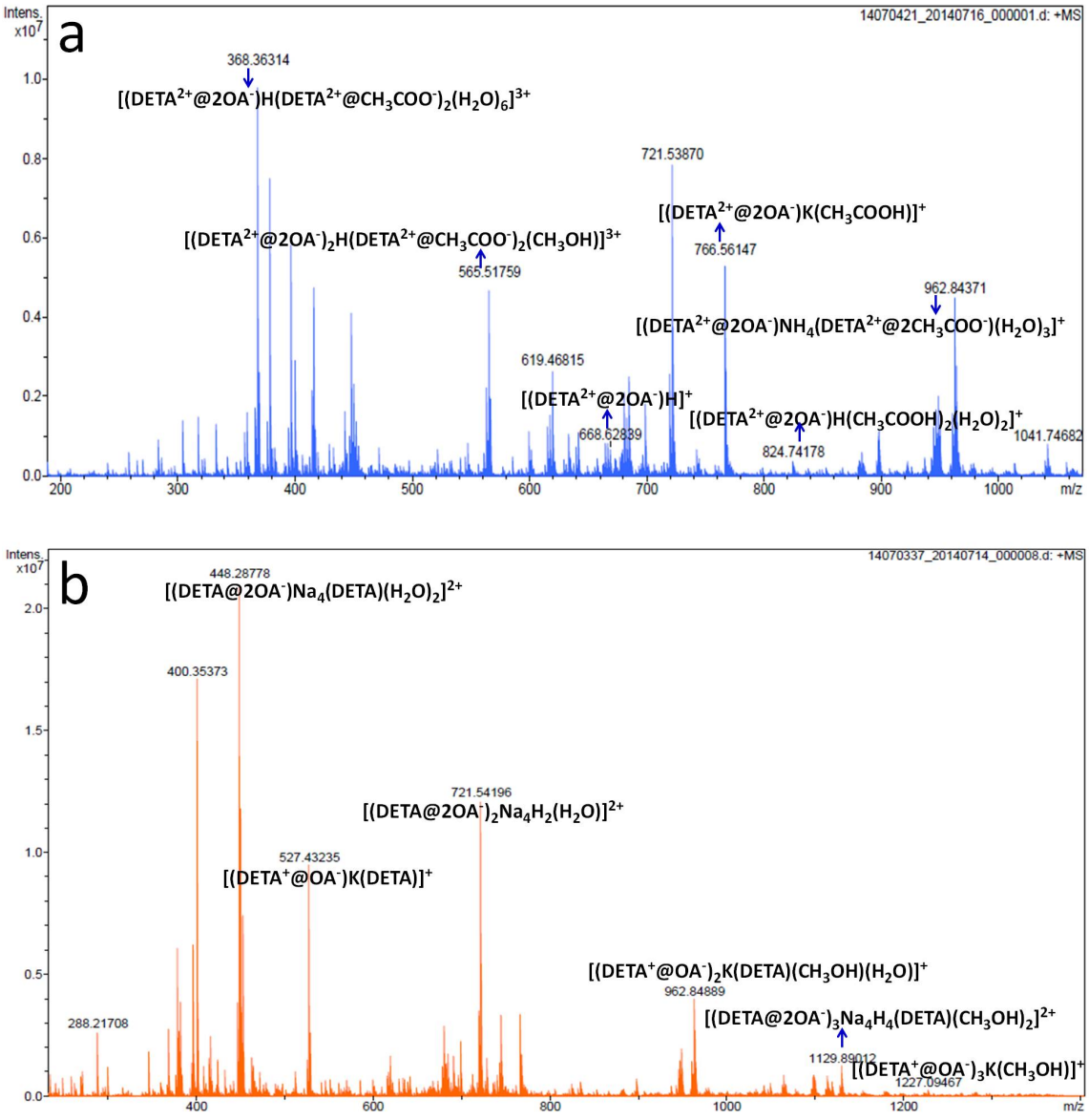


Figure S2 The DLS results of the OA/DETA sample at pH=9.0 in region I.

3. The MS results at three pH area.

In Figure S3a, the main MS peaks contained the same unit $DETA^{2+}$@$2OA^-$, which suggested that the main component formed in the OA/DETA mixed system in region I was $DETA^{2+}$@$2OA^-$. In addition, the height of the bilayer membranes from $DETA^{2+}$@$2OA^-$ is consistent with the AFM result. Therefore, it can be determined that the main building block in region I is $DETA^{2+}$@$2OA^-$. Similarly, in Figure S3b, there are a set of peaks corresponding to DETA@$2OA^-$ and $DETA^+$@OA^-, respectively, which demonstrates the existence of DETA@$2OA^-$ and $DETA^+$@OA^- in region II. In Figure S3c, a set of regular main peaks all contain the DETA@$2OA^-$,

suggesting that DETA@2OA$^-$ is the main building block in region III.



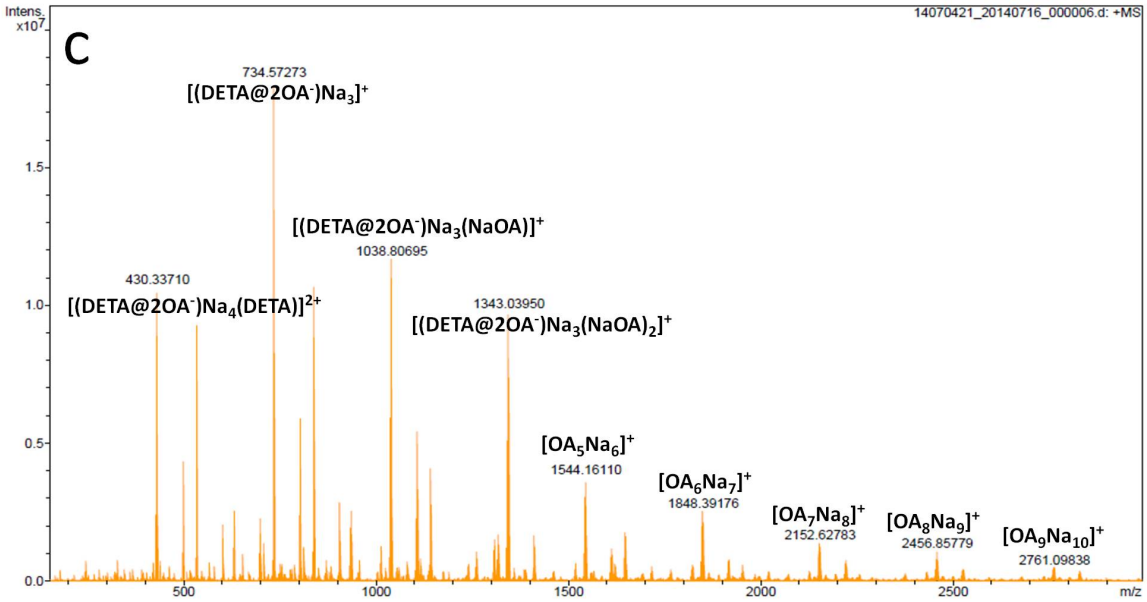
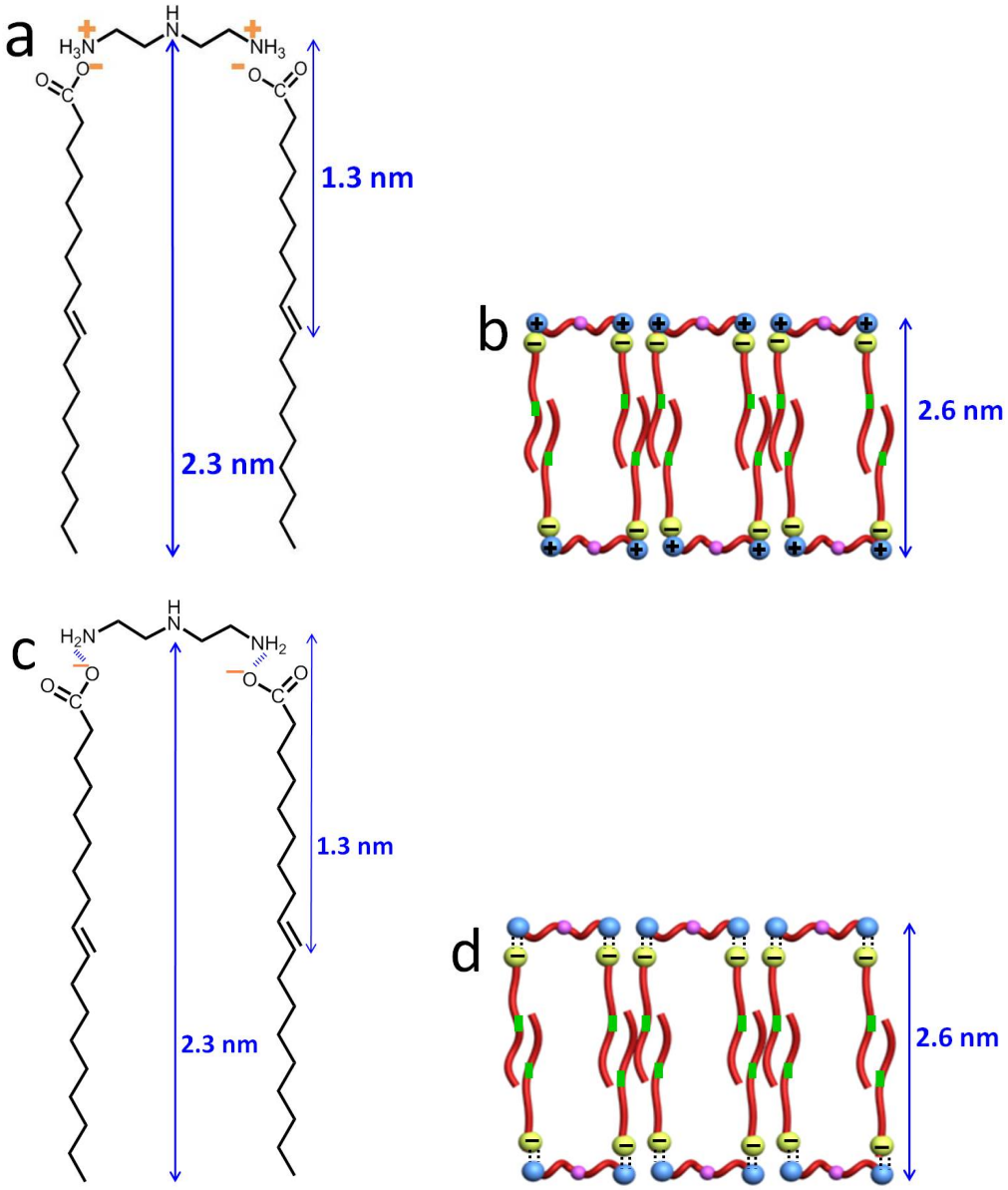


Figure S3 ESI-MS profiles of the OA/DETA mixed system at the different pH: a) pH=9.0, b) pH=10.5 and c) pH=12.0.

4. Calculation of the size of the building blocks

The extended length of the "pseudo Gemini surfactant" building blocks (a) estimated with Chem3D is around 2.3 nm. According to AFM results in Figure 4b, the height of the bilayer membranes of the unilamellar vesicle is 2.5 nm, which was formed by the building blocks (a). In addition, the length of the carbon chain from the double bond to the carbonyl group is about 1.3 nm. Thus it is presumed that the carbon chain of the oleic acid interdigitated until around the double bond as shown in Figure S4b, which is consistent with the results reported in the literature.[1, 2] Similarly, for the building blocks (c and g), the height of the bilayer membranes from them is about 2.6 nm (Figure S4d and h). For the building blocks (e), the extended length is about 3.1 nm according to the Chem3D results. Considering the presume that the carbon chain of the oleic acid interdigitated until around the double bond and the length of the carbon chain from the double bond to the carbonyl group is about 2.1 nm, the resultant bilayer membranes from the building blocks (e) is 4.2 nm.


a
1.3 nm
2.3 nm
b
2.6 nm
c
1.3 nm
2.3 nm
d
2.6 nm

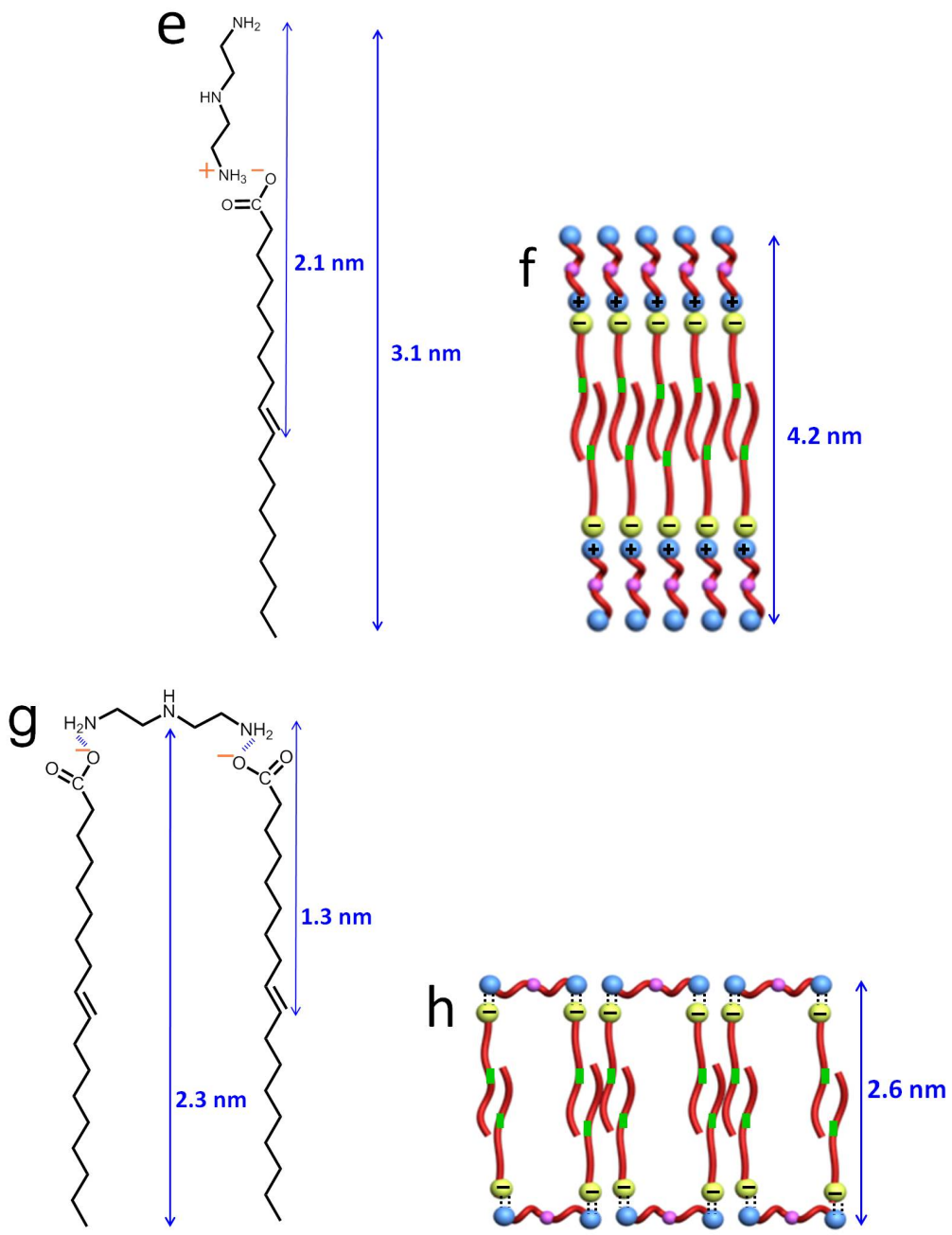


Figure S4 The building blocks of the OA/DETA mixed system at the different region: a) region I (8.0<pH<10.0), c) and e) region II (10.0<pH<11.5), g) region III (pH>11.5). And the schematic illustration of the possible aggregate behavior at the different region: b) region I, d) and f) region II, h) region III.

5. Addition of Urea validating the formation of "lamellaes.

In region II, the main molecular interactions of the OA/DETA mixed system are weak electrostatic attraction and hydrogen bonds. To make the self-assemblies clear, 5 M urea was added into the OA/DETA mixed system to destroy the hydrogen bonds.

After the addition of urea, the viscoelasticity of the mixed system significantly decreased from 2.7 to 1.0 Pa·s. The images in Figure 4b showed the existence of "lamellaes". Therefore, vesicles and "lamellaes" coexisted in region II.

6. The bilayers in region II.

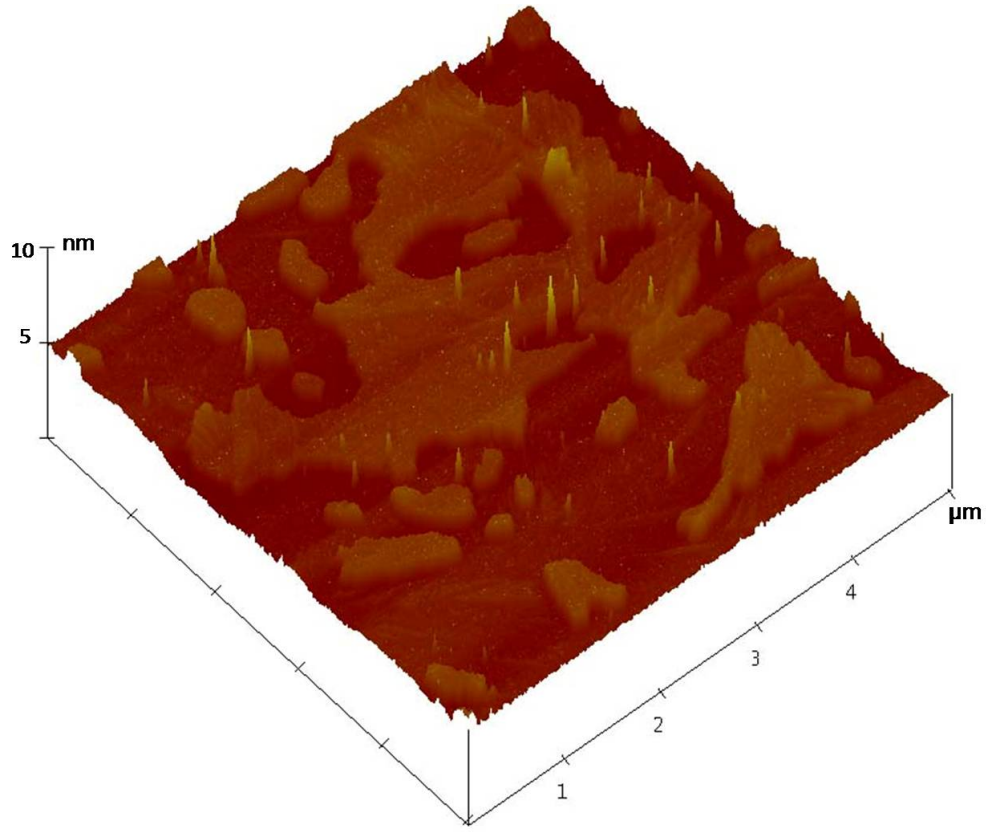


Figure S5 The surface plot of the OA/DETA mixtures at pH=11.1.

Notes and references

1. J. H. Jung, G. John, K. Yoshida and T. Shimizu, *J. Am. Chem. Soc.*, 2002, **124**, 10674-10675.
2. J. H. Jung, Y. Do, Y. A. Lee and T. Shimizu, *Chem-Eur J*, 2005, **11**, 5538-5544.