

# Supporting Information for

## Two-Step Adsorption of a Switchable Tertiary Amine Surfactant Measured

### Using Quartz Crystal Microbalance with Dissipation (QCM-D)

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The supporting information illustrated the various kinetics models used to fit the experimental adsorption results as well as the experimental results used to determine the critical micelle concentration.

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## 1. Kinetics Modeling

Many adsorption models have been developed to examine the kinetics and mechanism of adsorption reactions. In this study, a variety of kinetics model are fit to the experimental data through a non-linear least-square fitting method. The models using in this study are listed below. In the following equations,  $\Gamma$  is the adsorption at specific time  $t$ ,  $\Gamma_{\max}$  is the maximum adsorption (equilibrium adsorption),  $t$  is time,  $k_{ad}$  is adsorption kinetics constant and  $k_d$  is desorption kinetics constant.

( I ) Pseudo first and second order kinetics<sup>1,2</sup>

A pseudo first order rate equation and pseudo second order rate equation are showed below:

$$\text{First order: } \Gamma = \Gamma_{\max}(1 - e^{-k_{ad}t}) \quad (S1)$$

$$\text{Second order: } \Gamma = \frac{(k_{ad}Q_{\max}^2)t}{1 + k_{ad}Q_{\max}t} \quad (S2)$$

There are some assumptions of the models:

1. No interaction between the sorbed molecules and the surface is homogenous.
2. The maximum adsorption on the surface indicates there is saturated monolayer of adsorbates on the surface.

3. Assume the concentration of surfactant is constant.

4. Desorption rate is much lower than adsorption, which can be simplified as non-reversible process.

## ( II ) Langmuir kinetics<sup>1</sup>

The Langmuir kinetics is described by Langmuir in 1916. The assumptions are almost same as the pseudo reaction equation. However, the reversible reaction is not ignored in Langmuir model, which indicated that desorption rate needs to be considered compared to the adsorption rate. The rate equation is shown below:

$$\Gamma = \Gamma_{max} \left( \frac{k_{ad}}{k_{ad} + k_d} \right) (1 - e^{-(k_{ad} + k_d)t}) \quad (S3)$$

From our fitting results, we found that the desorption kinetics constant is much smaller than adsorption kinetics constant. Thus, we could assume that desorption process can be neglected.

## ( III ) Elovich <sup>1</sup>

The Elovich's equation was presented by Zeldowitsch in 1934, the rate equation is shown below:

$$\Gamma = \frac{1}{\beta} \ln (1 + \alpha \beta t) \quad (S4)$$

In eq. (4),  $\alpha$  is initial sorption rate and  $\beta$  is a constant related to surface coverage and adsorption activation energy. The Elovich equation is usually used to understand the adsorption of gas molecule onto solid surface. However, recently the equation also successfully applied to describe some specific adsorption process in aqueous solutions.

The assumption of Elovich included:

1. The interaction between molecules is considered.
2. The adsorption energy is in proportion to the surface coverage.
3. The concentration of surfactant in bulk phase is assumed to be constant.

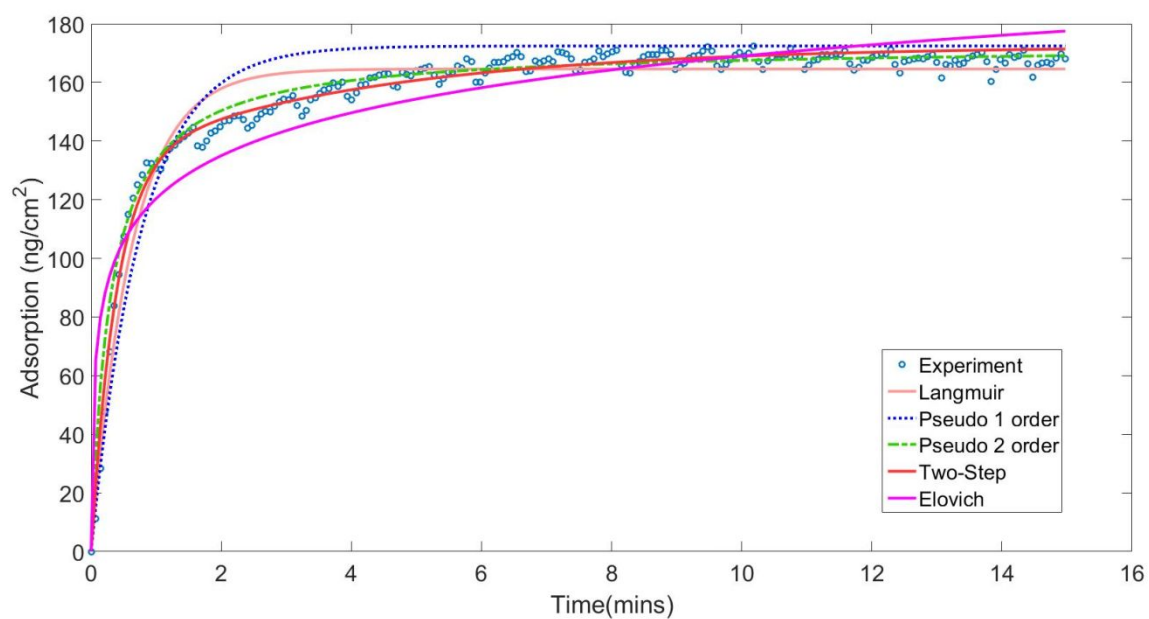
#### (IV) Two-step first-order kinetics<sup>3-5</sup>

Biswas and Chattoraj previously studied the kinetics of adsorption of cationic surfactant, hexadecyl trimethyl ammonium bromide (CTAB), and first found that the adsorption followed a two-step first-order model.<sup>5</sup> After that, Tabor et al. provided a fully developed and detailed equation to describe the theoretical adsorption model for the surfactant.<sup>6</sup> The diffusion of the molecules and the adsorption reaction are considered in the two-step first-order kinetics model. However, it is hard to determine certainly what the two rates represents through single mathematic model.

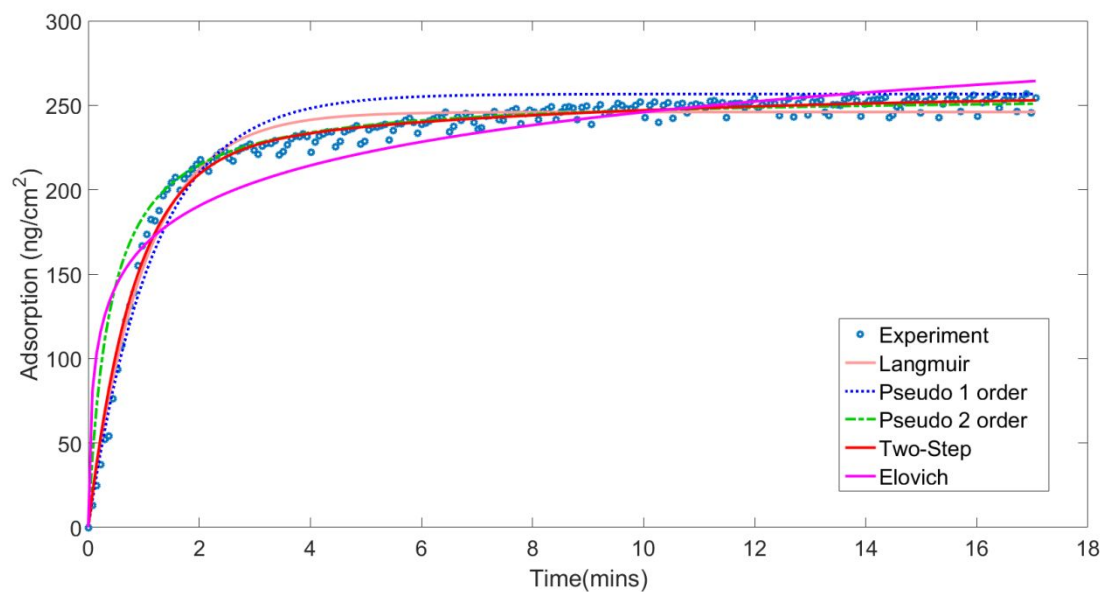
Different mechanisms are proposed to explain the two subsequent rates, such as the ratio of inhomogeneous surface sites, formation of aggregation of the adsorbed molecules or the rearrangement of surfactant results in additional binding sites. The equation of two-step first-order kinetics is showed in eq (5).  $A_1$  and  $A_2$  is pre-exponential terms while  $k_{ad1}$  and  $k_{ad2}$  are the rate constants for the two sequential processes.

$$\Gamma = \Gamma_{max} - A_1 e^{-k_{ad1}t} - A_2 e^{-k_{ad2}t} \quad (S5)$$

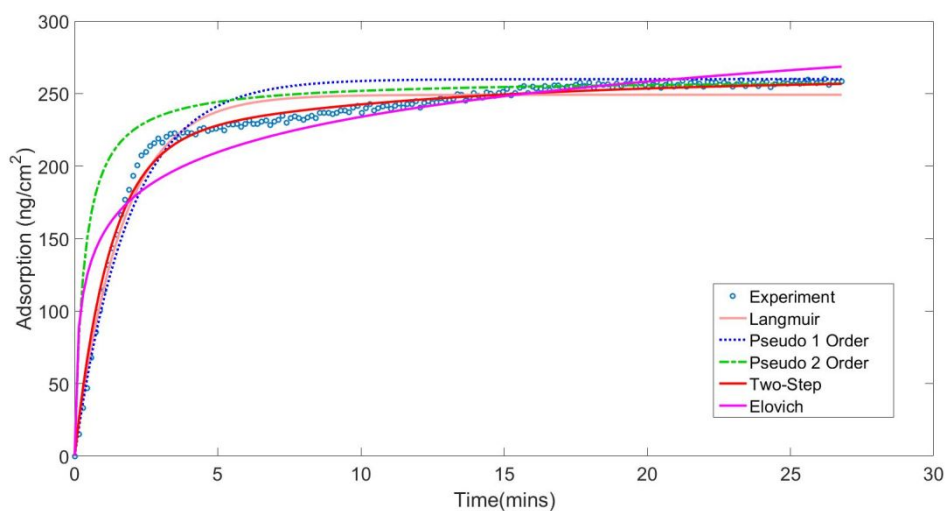
The results, calculated from above different kinetics models, are used to compare with the experimental results, which showed below in Figure S1 to Figure S3. The results show that the two-step adsorption model is the best fitting model to describe the adsorption behavior of TTM.



**Figure S1.** Experimental and Modeling results of TTM adsorption under 0.01M NaCl, pH3



**Figure S2.** Experimental and Modeling results of TTM adsorption under 0.01M NaCl, pH5

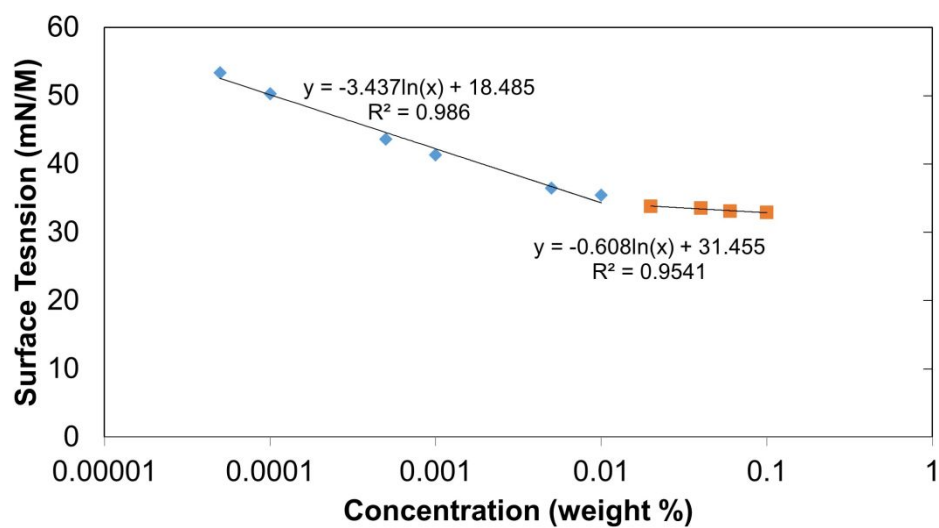


**Figure S3.** Experimental and Modeling results of TTM adsorption under 0.01M NaCl, pH7

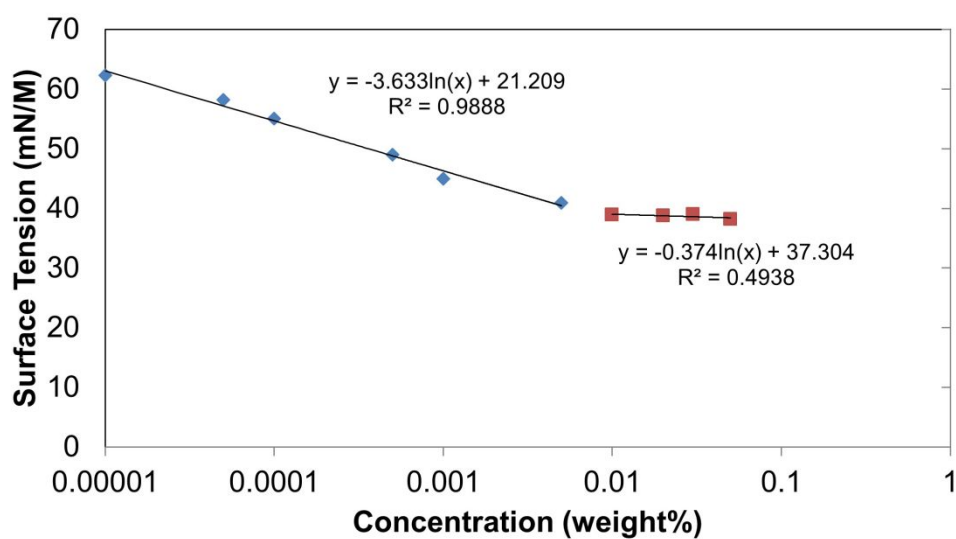
## 2. Critical micelle concentration

	pH=7	pH=5	pH=3
0.1 M NaCl	0.0102%	0.0076%	0.00208%
0.01 M NaCl	0.0018%	0.0012%	0.00086%
0.001 M NaCl	0.00135%	0.00149%	0.00080%

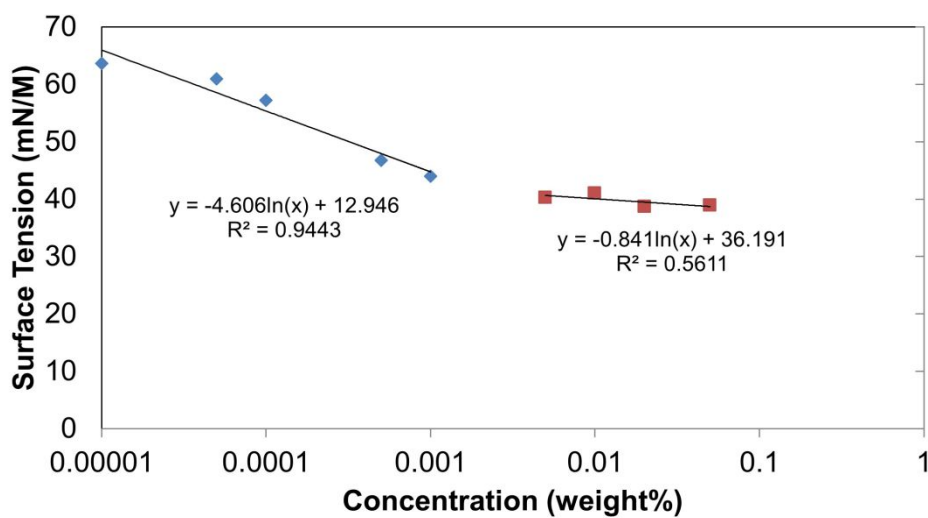
**Table S1.** The critical micelle concentration of TTM under different conditions



(a) pH=7



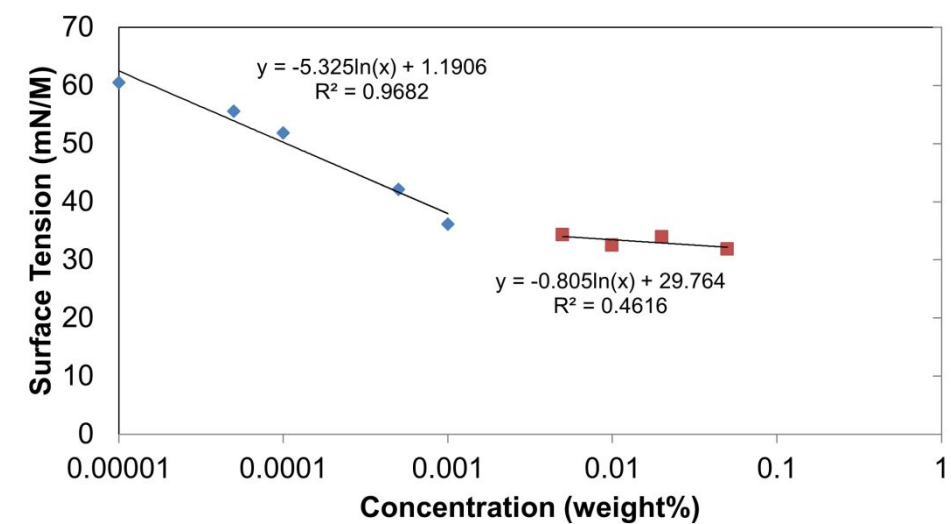
(b) pH=5



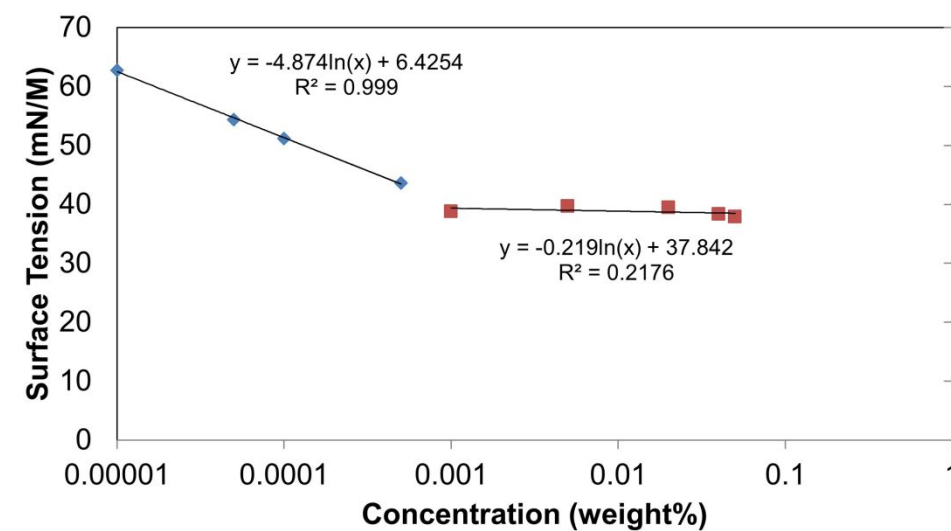
(C) pH=3

Figure S4. Critical micelle concentration of TTM under 0.1M NaCl (a) pH=7 (b) pH=5 (C) pH=3

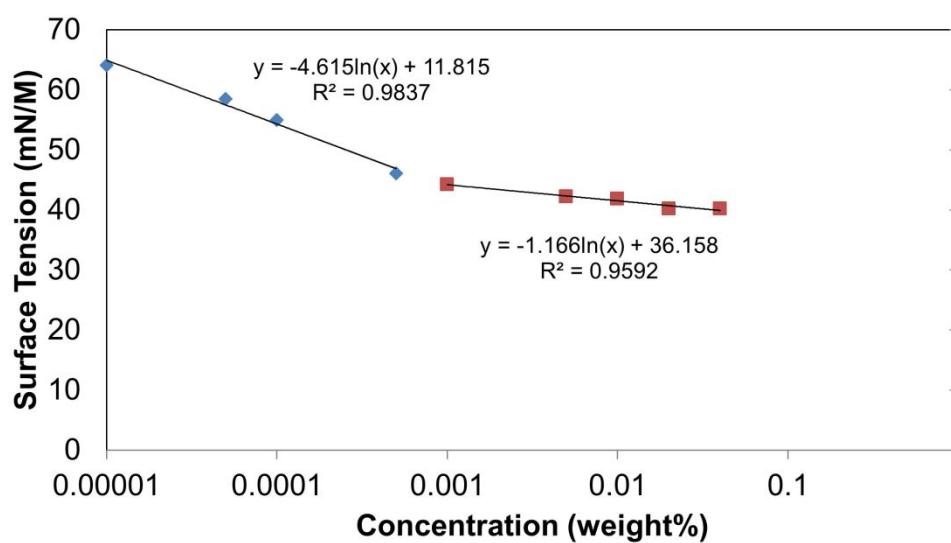




(a) pH=7

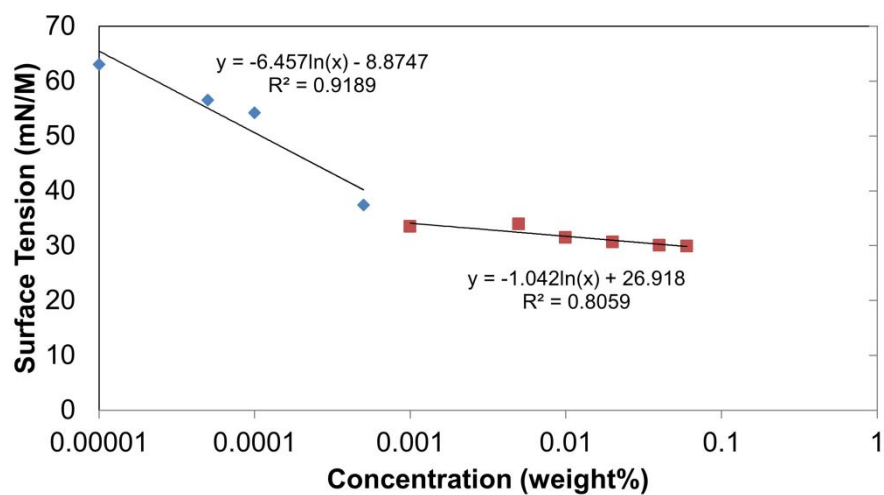


(b) pH=5

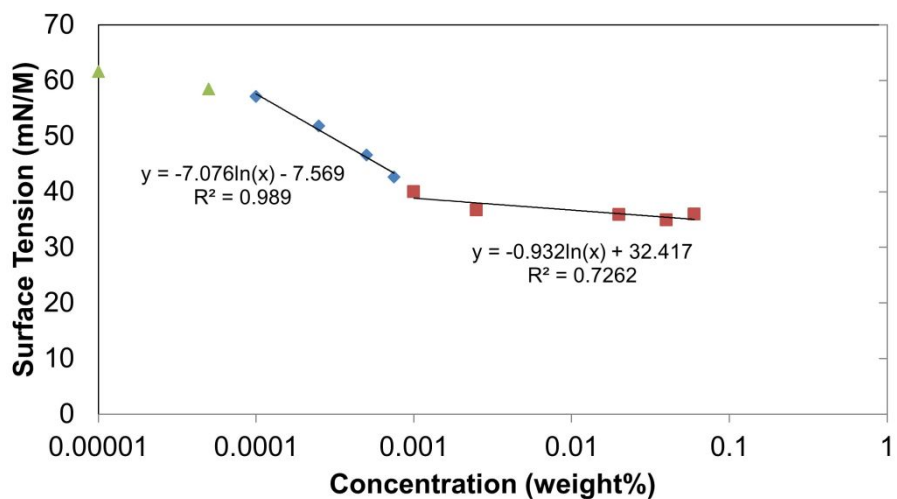


(C) pH=3

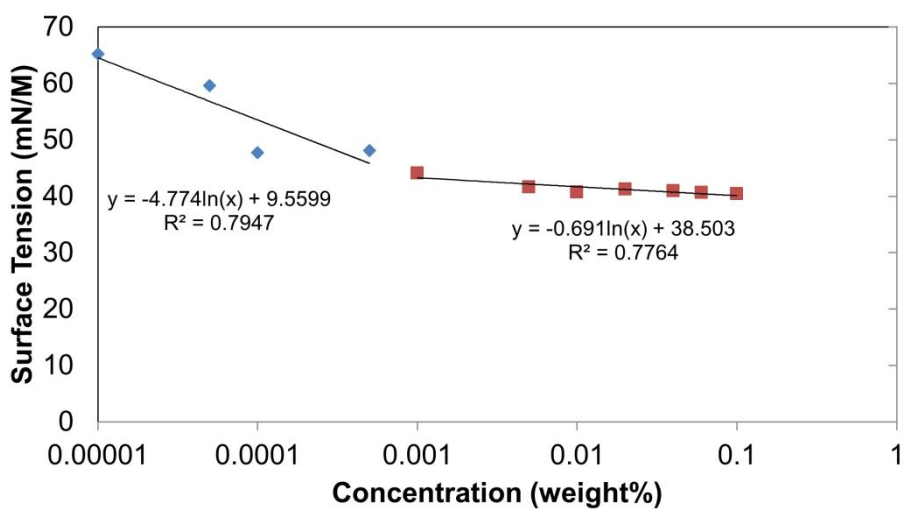
**Figure S5.** Critical micelle concentration of TTM under 0.01M NaCl (a) pH=7 (b) pH=5 (C) pH=3



(a) pH=7



(b) pH=5



(C) pH=3

**Figure S6.** Critical micelle concentration of TTM under 0.001M NaCl (a) pH=7 (b) pH=5 (C) pH=3

## References

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