Electronic Supplementary Information (ESI) for

Responsive morphology transition from micelles to vesicles based on dynamic covalent surfactant

Pengxiang Wang,[a,b,c] Tongyu Zhu,[a,b] Xiaoyu Hou,[a,b] Yilu Zhao,[a,b] Xiangfeng Zhang,[a,b] Hongbin Yang,[*,a,b] and Wanli Kang[*,a,b]

[a] *Shandong Key Laboratory of Oilfield Chemistry, School of Petroleum Engineering, China University of Petroleum (East China), Qingdao 266580, P. R. China.*

[b] *Key Laboratory of Unconventional Oil & Gas Development (China University of Petroleum (East China)), Ministry of Education, Qingdao, 266580, P.R. China.*

[c] *School of Mining & Petroleum Engineering, University of Alberta, Edmonton, Alberta, T6G 2V4, Canada.*

[*] Corresponding author. Email address: hongbinyang@upc.edu.cn (H. Yang); kangwanli@126.com (W. Kang)

Experimental：

Calculation of species distribution

The dissociation constant (pK_a) of HB and OA are found at 7.61 and 10.65 respectively at 25℃ on a website (https://www.chemicalbook.com). As a monobasic acid, the HB has two states of natural and deprotonation (HB^-) at the same pH, and the distribution of the species at different pH conditions can be calculated by the equation 1-2:

$$[\mathrm{HB}]\% = \frac{c_{[\mathrm{H}^+]}}{K_\mathrm{a} + c_{[\mathrm{H}^+]}} \times 100\% \tag{1}$$

$$[\mathrm{HB}^-]\% = \frac{K_\mathrm{a}}{K_\mathrm{a} + c_{[\mathrm{H}^+]}} \times 100\% \tag{2}$$

As we know, the K_a and $c_{[H^+]}$ can be calculated from pK_a and pH value by the following equations:

$$pK_a = -\lg K_\mathrm{a} \tag{3}$$

$$pH = -\lg c_{[\mathrm{H}^+]} \tag{4}$$

According to the above formula, we can calculate the species distribution of HB at different pH, and the species distribution of OA is calculated using the same method.

$$[\mathrm{OA}]\% = \frac{K_\mathrm{a}}{K_\mathrm{a} + c_{[\mathrm{H}^+]}} \times 100\% \tag{5}$$

$$[OA^+]\% = \frac{c_{[H^+]}}{K_a + c_{[H^+]}} \times 100\% \quad (6)$$

The species distribution calculation of CTAB/HB/OA solution is more complicated due to the fabrication of HB-OA, and the HB and OA are present as HB, HB^-, OA, OA^+ (protonated OA), HB-OA and HB-OA^- (deprotonatated HB-OA) in this condition. However, the relationship between the conversion of surfactant and pH (X_{pH}) can be concluded in equation 7 from the results of ^{1}H NMR:

$$S\% = (0.0452 X_{pH}^5 - 1.7915 X_{pH}^4 + 26.6361 X_{pH}^3 - 182.3109 X_{pH}^2 + 574.0762 X_{pH} - 663.9291) \times 100\% \quad (7)$$

Besides, the ability of HB and HB^- to form the anionic surfactant through the imine bond is equally. Therefore, the content of HB-OA and HB-OA^- can be calculated by equation 6 and 7:

$$[HB\text{-}OA]\% = S\% * [HB]\% \quad (8)$$

$$[HB\text{-}OA^-]\% = S\% * [HB^-]\% \quad (9)$$

And the residual HB and HB^- at different pH can be calculated by the following equations:

$$R_{[HB]}\% = [HB]\% - [HB\text{-}OA]\% \quad (10)$$

$$R_{[HB^-]}\% = [HB^-]\% - [HB\text{-}OA^-]\% \quad (11)$$

For the residual OA, it is also divided into protonated and natural states, and in accordance with the distribution of equations 5 and 6. So the species distribution of OA was obtained from equation 12 and 13:

$$R_{[OA]}\% = (1 - S\%) * [OA]\% \quad (12)$$

$$R_{[OA^+]}\% = (1 - S\%) * [OA^+]\% \quad (13)$$

Additional Results:

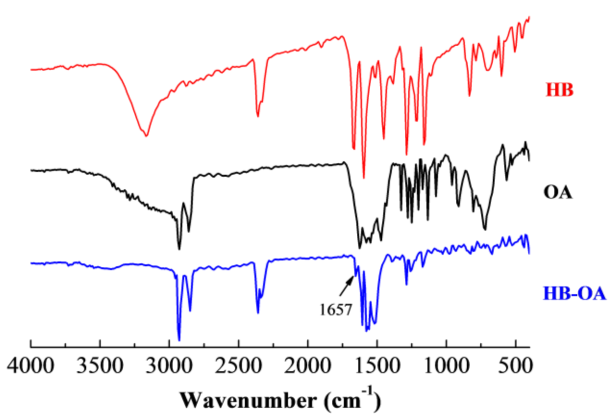


Fig.S1 FTIR spectra of HB (red), OA (black), and HB-OA (blue).

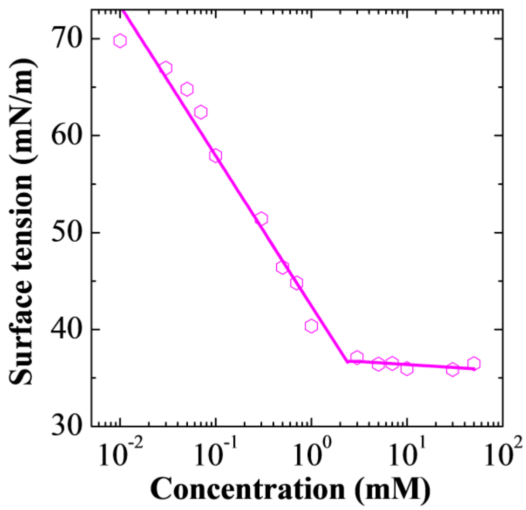


Fig.S2 Variation in surface tension with concentration of HB-OA at pH 12.02 and 25℃.

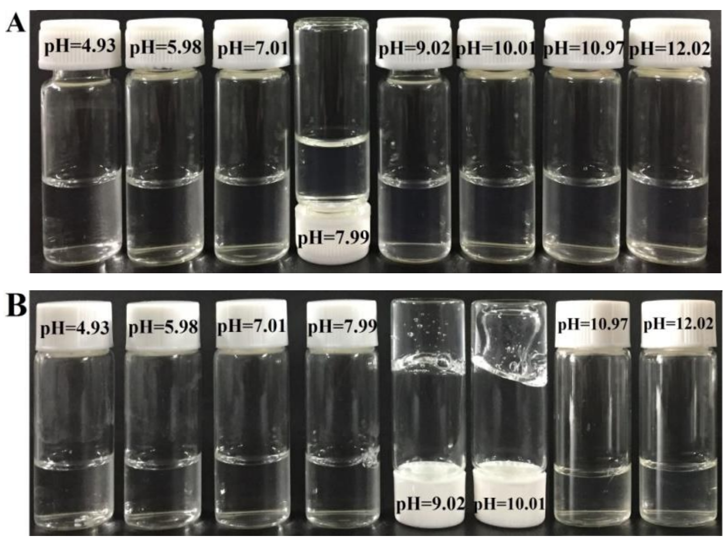


Fig.S3 Macroscopic appearance of (A) CTAB/HB and (B) CTAB/phenol aqueous solution at various pH and 25°C.

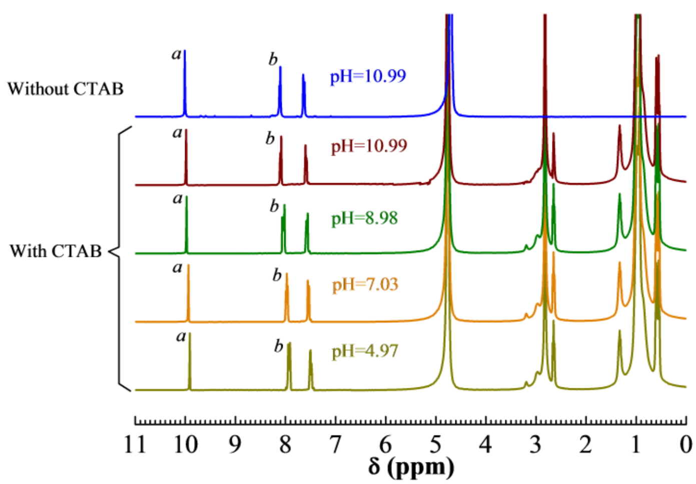


Fig.S4 The ^{1}H NMR spectra of CTAB/HB at different pH and 25°C.

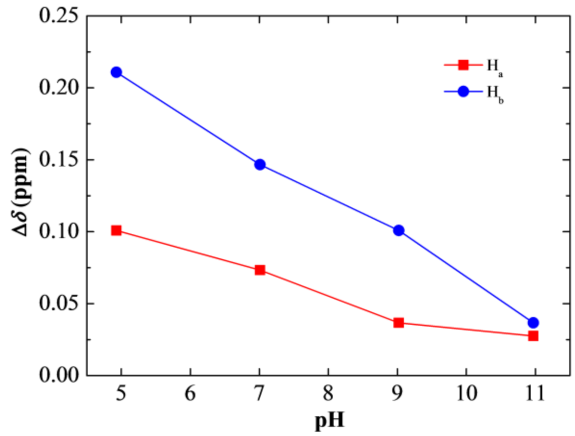


Fig.S5 Variation of chemical shift change $\Delta\delta$ on the proton b at different pH.

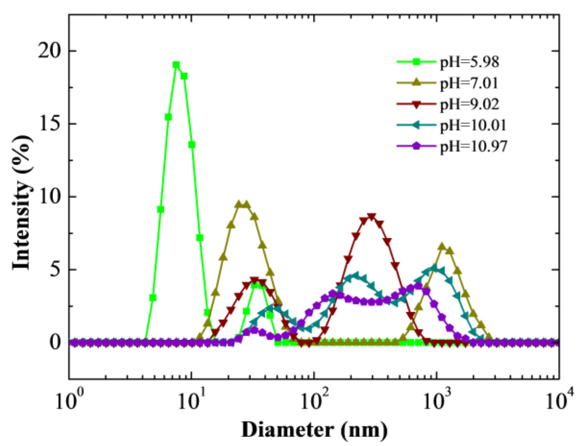


Fig.S6 Effects of pH on the hydrodynamic diameter of the aggregates at 25℃.

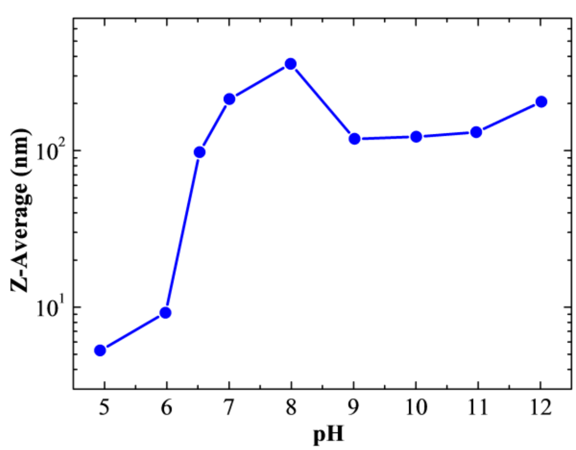


Fig.S7 Effects of pH on the average diameter size at 25℃.

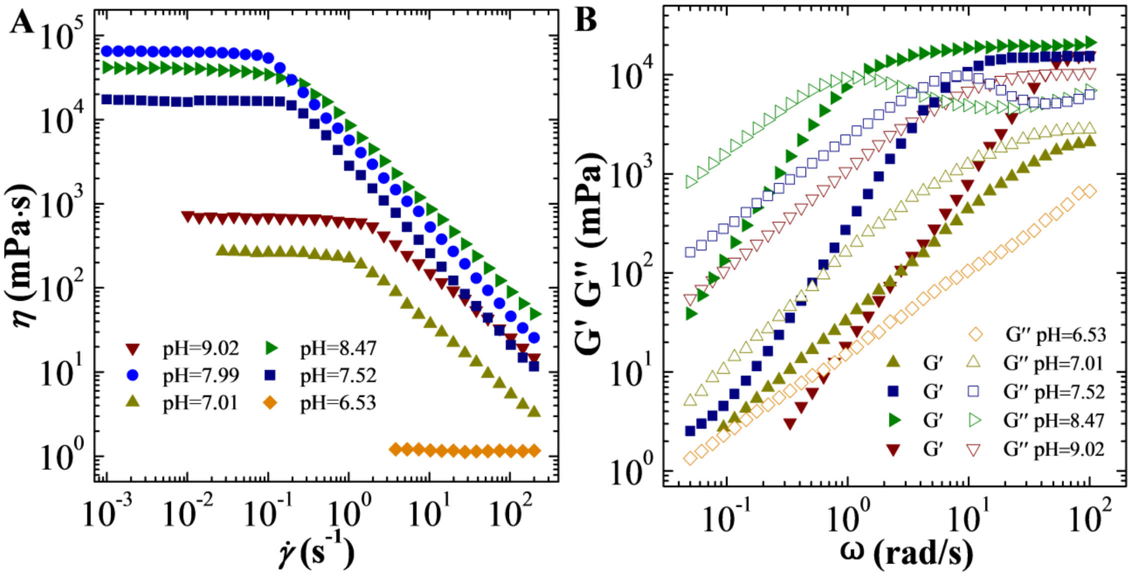


Fig.S8 Steady (A) and dynamic (B) rheological behaviors of CTAB/HB/OA solutions at different pH and 25 °C.

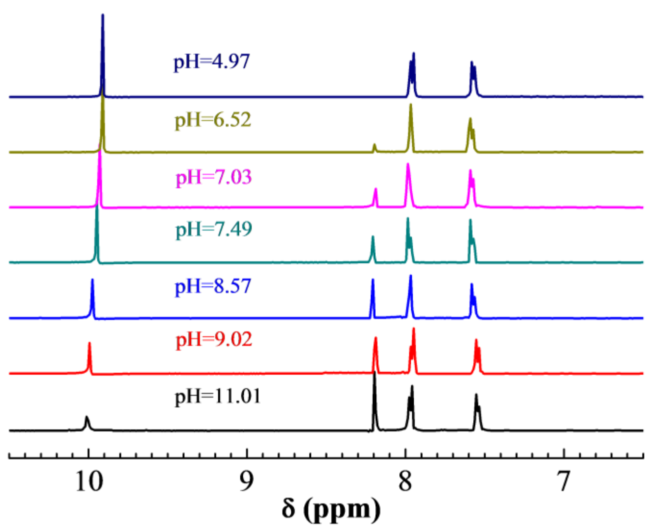


Fig.S9 The ^{1}H NMR spectra of CTAB/HB/OA at different pH and 25°C.

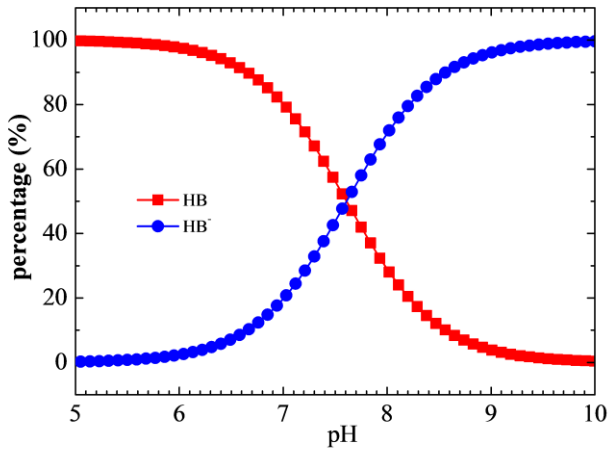


Fig.S10 Species distribution resulting from an aqueous solution of HB at 25 ℃.

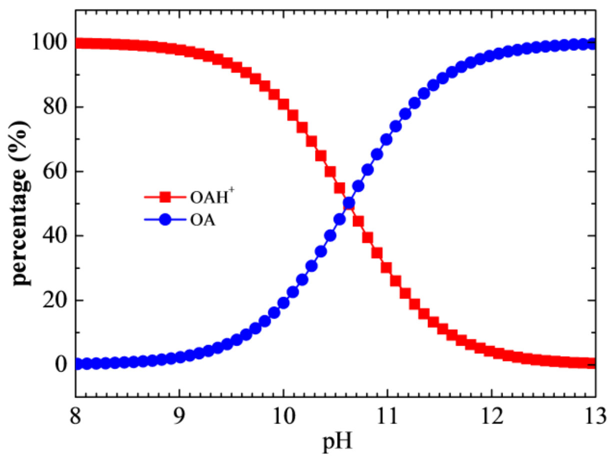


Fig.S11 Species distribution resulting from an aqueous solution of OA at 25 ℃.

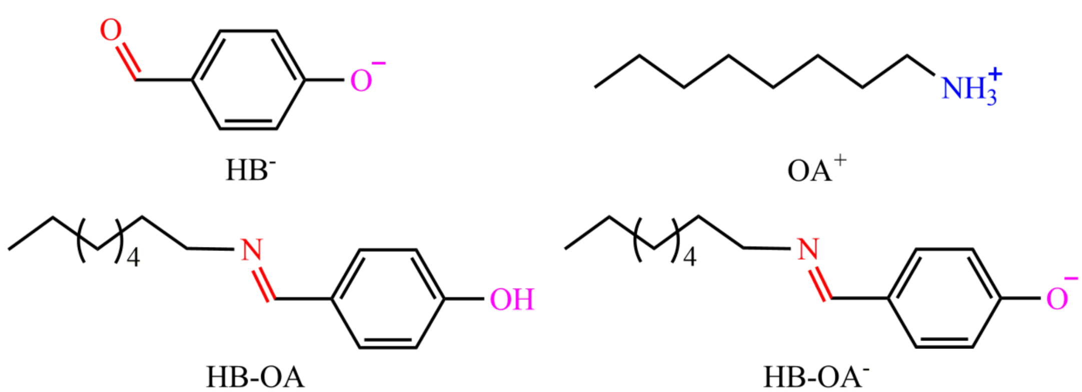


Fig.S12 Chemical structures of HB^-, OA^+, HB-OA and $HB\text{-}OA^-$.

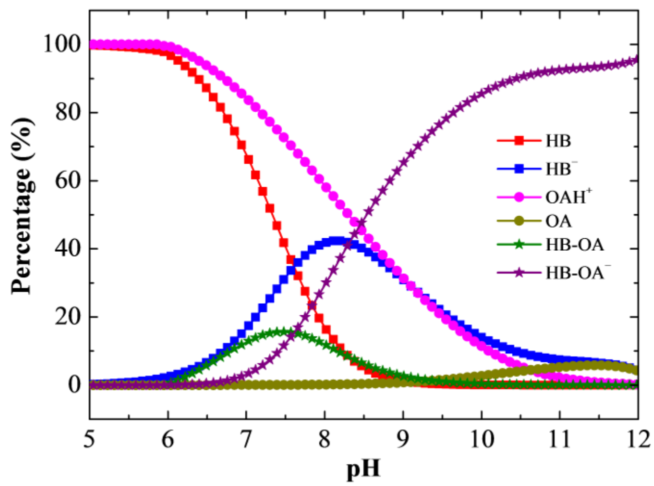


Fig.S13 Species distribution resulting from an aqueous solution of HB/OA at 25 ℃.

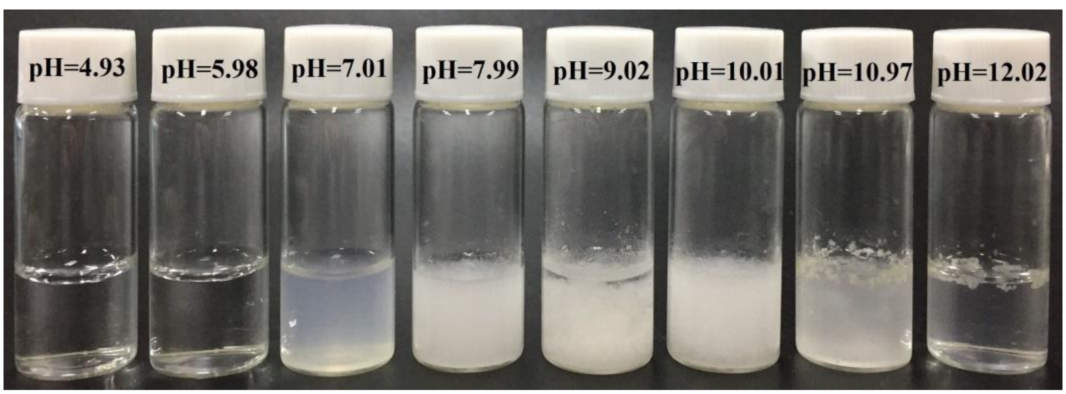
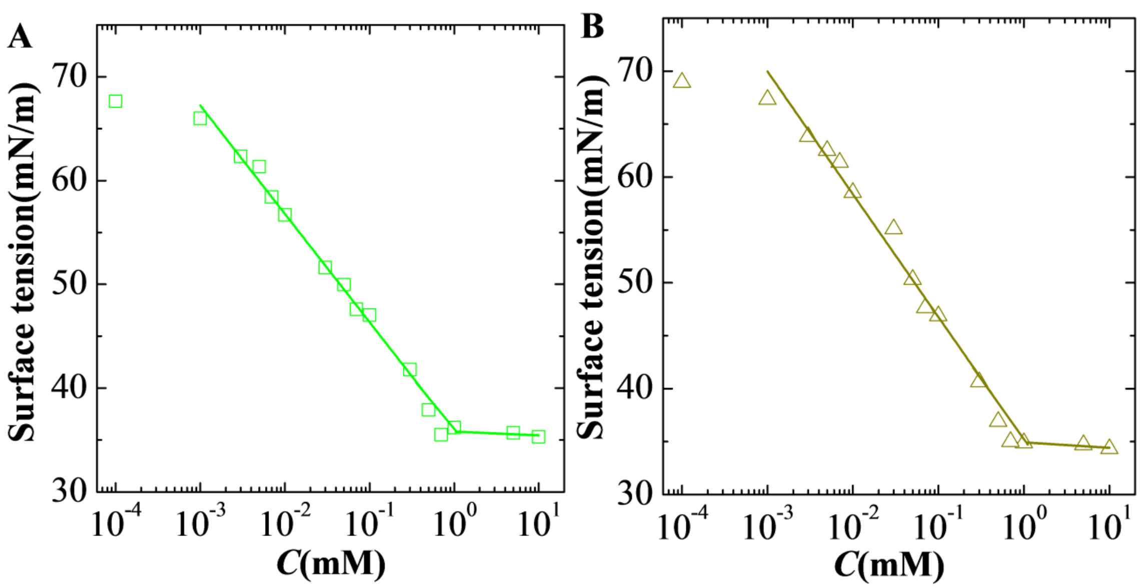


Fig.S14 Macroscopic appearance of HB/OA aqueous solution at various pH and 25°C.



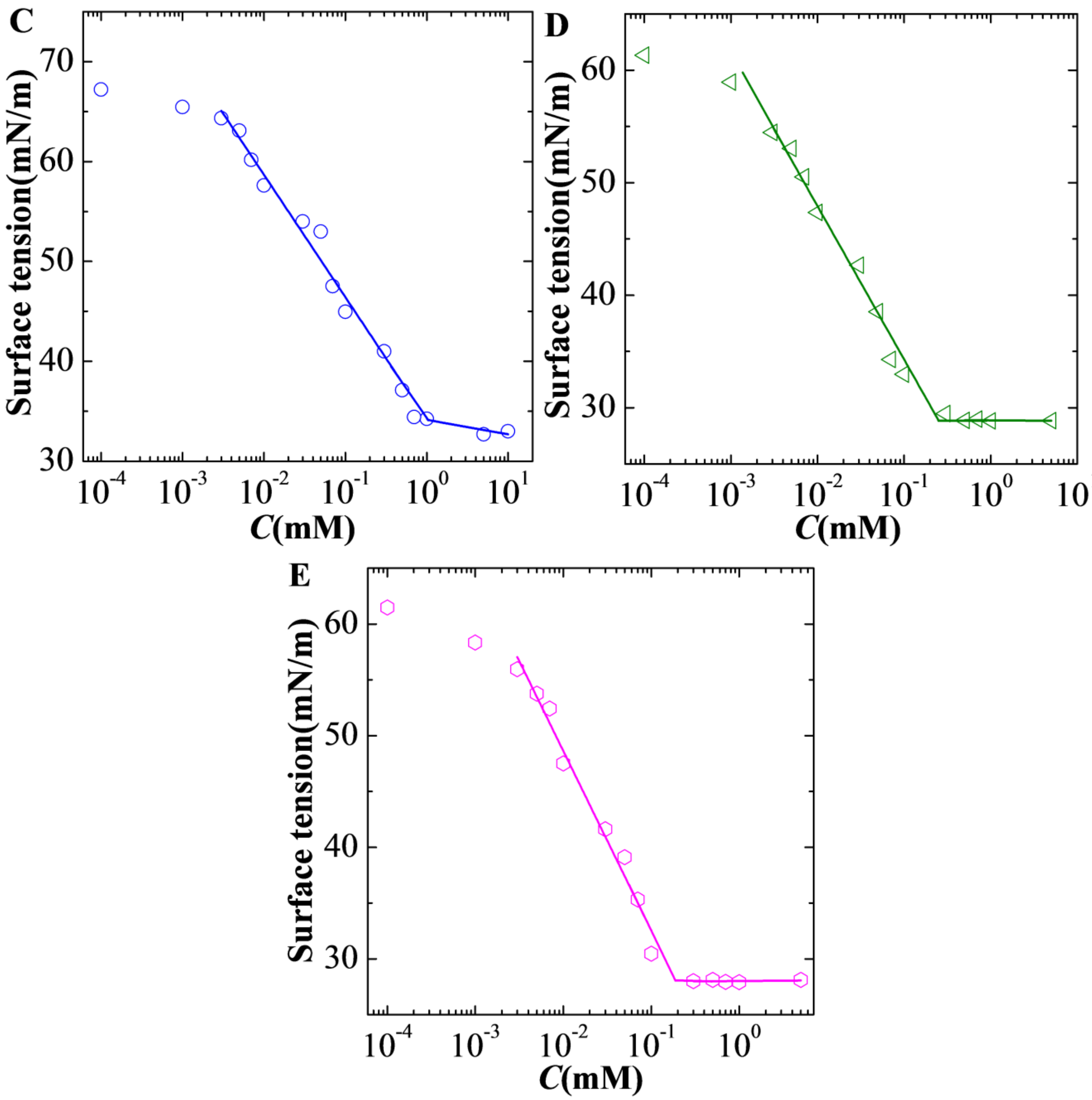


Fig.S15 Variation in surface tension with concentration of CTAB/HB/OA at (A) pH=5.98, (B) pH=7.01, (C) pH=7.99, (D) pH=10.01, (E) pH=12.02, and

25℃.