Supporting Information

for

Simulating pH titration of a single surfactant in ionic and nonionic micelles

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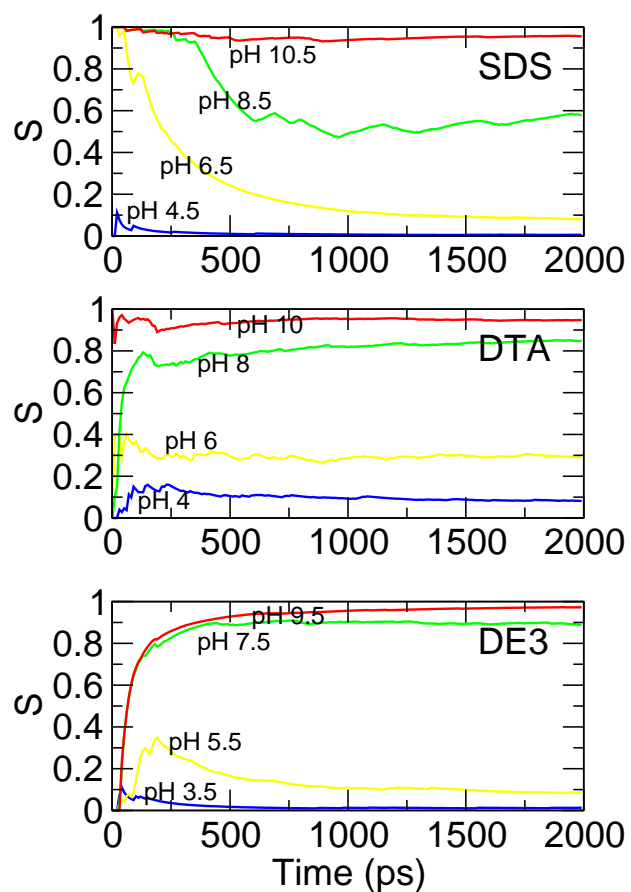
Figure S1: Cumulative unprotonated fraction of lauric acid in the SDS, DTA, and DE3 micelles from the explicit-solvent titration simulations. For each micelle S values are shown at 2 pK unit intervals as indicated.
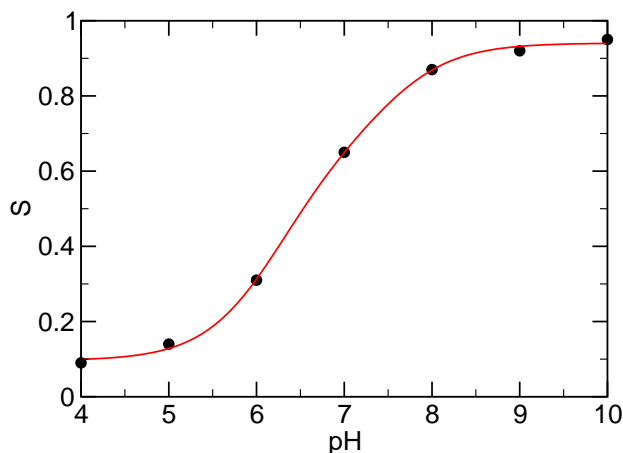
Figure S2: Titration data for lauric acid in the DTA micelle, fit to a linear combination of modified Hill equations.

The titration data for lauric acid in DTA can be fit to a linear combination of two modified Hill equations (Eqn 9 in Ref. (1)):

$$S = x \left(\frac{s_{A^-} + s_{HA} 10^{n(pK_{a,1} - pH)}}{1 + 10^{n(pK_{a,1} - pH)}} \right) + (1 - x) \left(\frac{s_{A^-} + s_{HA} 10^{n(pK_{a,2} - pH)}}{1 + 10^{n(pK_{a,2} - pH)}} \right) \tag{1}$$

where s_{A^-} and s_{HA} are fitting parameters, which represent the S values at extreme pH conditions, $pK_{a,1}$ and $pK_{a,2}$ represent the pK_a of lauric acid in two distinct conformational states, and x denotes the relative population of the two states. When we fit the titration data to Eqn. 1 with $n = 1$, we obtain the fit shown in Fig. S2, with $pK_{a,1} = 7.4$, $pK_{a,2} = 6.2$, and $x = 0.33$. This indicates that the lauric acid molecule experiences two distinct conformational states due to fluctuations of the DTA micelle, with the lower-pK_a state dominating, and the exchange between these states is slow relative to the simulation time. When the titration data is fit to a single Hill equation, the result is a pK_a of 6.5, with a Hill coefficient of 0.5.

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References

1. Wallace, J. A.; Shen, J. K. *J. Chem. Theory Comput.* **2011,** *7,* 2617–2629.