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## Supporting Information

### Quantitative description of surface adsorption of surfactant in aqueous solution without the Gibbs equation

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Determination of parameter $\beta_k$ in the polynomial function $f$ and the thickness of surface layer $h$.

The equations needed here are from the original paper and their labels are also changed as follows

$$\gamma = \gamma_0 + \frac{vRT}{A_{sm}} \ln a_B^s \tag{S1}$$

$$\gamma = \gamma_1 - vRThc_B^\alpha f \ln(f) + vRTh \sum_{k=2}^{m+1} \frac{k-1}{k} \beta_{k-1}(c_B^\alpha)^k \tag{S2}$$

$$A_{ma} = |A_{sm}|/N_A \tag{S3}$$

$$A_{ma} = A_s/(n_B^s N_A) = 1/(c_B^s h N_A) \tag{S4}$$

where $\gamma$, $T$, $h$ and $R$ are the surface tension, temperature, surface thickness of the solution and gas constant. The superscript s and $\alpha$ are symbols to denote separately surface and bulk phases. $c$ is the surfactant concentration of solution. $\gamma_0$ and $\gamma_1$ are the integration constant. $N_A$ is Avogadro constant. $A_{ma}$ is the molecular area of surfactant.

In order to get an optimal thickness $h_{opt}$, the following procedure is proposed:

(A) Fit $\gamma$ and $c_B^\alpha$ with eqn (S2) for a certain $h$, then calculate $c_B^s$ using $c_B^s = fc_B^\alpha$ and the molecular area $A_1$ with eqn (S4).

(B) Fit $\gamma$ and $c_B^s$ with Eqn (S1) and calculate the molecular area $A_2$ with eqn (S3).

(C) If the difference of $A_1$ and $A_2$ is smaller than some given criterion, the given $h$ will be $h_{opt}$ and $A_1$ (or $A_2$) will be the molecular area $A_{ma}$, and the procedure will be stopped. Otherwise, go to the step (A) with another $h$ until the threshold for the difference of $A_1$ and $A_2$ is reached.

The surfactant OTABr is taken as an example to show how $\beta_k$ and $h$ could be calculated step by step with the procedure described above. The data of surface tension of OTABr at different concentrations [1] is listed in the Table S1.

**Table S1.** The surface tension of OTABr at different concentration. $c$ is the concentration of surfactant, $\gamma$ is the surface tension.

| $c$ (mol/L) | 0.02 | 0.04 | 0.06 | 0.08 | 0.10 | 0.12 | 0.14 | 0.16 |
|---|---|---|---|---|---|---|---|---|
| $\gamma$ (mN/m) | 69.4 | 63.1 | 59.5 | 54.6 | 51.1 | 48.9 | 46.5 | 44.0 |
| $c$ (mol/L) | 0.18 | 0.20 | 0.30 | 0.40 | 0.50 | 0.60 | 0.80 | 1.00 |
| $\gamma$ (mN/m) | 41.7 | 39.8 | 36.4 | 35.8 | 35.5 | 35.4 | 35.2 | 35.1 |

The three-step procedure described above is used for fitting. At step (A), $m$ in Eqn(S2) is assumed to be 2, which is sufficient for the present problem. Thus, Eqn (S2) becomes

$$\gamma = \gamma_1 - vRTh(c_B^\alpha f \ln(f) - \frac{1}{2}\beta_1(c_B^\alpha)^2 - \frac{2}{3}\beta_2(c_B^\alpha)^3) \tag{S5}$$

where $f = \beta_0 + \beta_1 c_B^\alpha + \beta_2 (c_B^\alpha)^2$. The first 13 points in Table S1 are used for fitting. The last three points are not considered in the fitting procedure because the variation of surface tension of these points is very small. The

guess interval for $h$ is chosen to be [0.1nm,5.0nm] which is big enough for the present study. We then get 50 values of $h$ including two boundary points, which divide the interval into 49 sub-intervals. For each fixed $h$ we performed the nonlinear fitting according to the Eqn (S5) using the curve_fit() function in the optimize module of SciPy [2]. The trust region reflective algorithm [3] was applied to get the corresponding $\beta_0$, $\beta_1$ and $\beta_2$. After fitting,

we obtain 50 sets of $\beta_0$, $\beta_1$ and $\beta_2$. We then calculate the surface concentration of OTABr with $c_B^{\mathrm{s}} = f c_B^{\alpha}$ for the

first 13 points listed in Table S1. Finally, we compute the molecular area $A_1$ with Eqn (S4) at the saturated point. The saturated concentrations of OTABr, HTABr and DTABr are 0.5 mol/L, 1.3 mol/L and 0.08 mol/L, respectively.

At step (B), Using each set of $c_B^{\mathrm{s}}$ data obtained from step (A), we fit $\gamma$ and $c_B^{\mathrm{s}}$ with eqn (S1) and calculate

the molecular area $A_2$ with Eqn (S3) without the first 2 points with lower concentrations.

At step (C), If the difference of $A_1$ and $A_2$ for some $h$ is smaller than the criterion $10^{-2}$ square angstroms ($\text{Å}^2$), we stop the procedure and the given $h$ is considered to be $h_{\mathrm{opt}}$ and $A_1$ (or $A_2$) will be the molecular area $A_{\mathrm{ma}}$. Otherwise, we have to get another interval of $h$ by comparing the differences of all sets of $A_1$ and $A_2$. For OTABr, we found that: for $h$ = 4.8 nm, $A_1$ = 34.609 $\text{Å}^2$ and $A_2$ = 34.429 $\text{Å}^2$; for $h$ = 4.9 nm, $A_1$ = 34.330 $\text{Å}^2$ and $A_2$ = 34.455 $\text{Å}^2$. If we connect two points (4.8, $A_2$=34.429) and (4.9, $A_2$ = 34.455) with a line segment, and (4.8, $A_1$ = 34.609) and (4.9, $A_1$ = 34.330) with another line segment. The two line segments have a cross point. Thus, the $h_{\mathrm{opt}}$ must lie between 4.8 and 4.9 nm. The new interval is [4.8nm, 4.9 nm]. This is our empirical rule. Once the new interval is determined, we then go to step (A) and repeat the procedure until the difference of $A_1$ and $A_2$ is less than the criterion $10^{-2}$ $\text{Å}^2$. The final results are listed in Table S2, which including various parameters of the three surfactants.

The simulation results for HTABr, OTABr and DTABr are listed in Table S2. As can be seen from the table, $h_{\mathrm{opt}}$ is a simulation parameter in eqn (S2) and (S5), and may not be the true value of the thickness of surface layer. However, like the length of alkyl chain, a large magnitude of $h_{\mathrm{opt}}$ indicates a strong capability of lowering the surface tension of pure water.

**Table S2.** Various parameters of three surfactant solutions.

| Surfactant | $h_{\mathrm{opt}}$/nm | $\beta_0$ | $\beta_1$/L·mol$^{-1}$ | $\beta_2$/L$^2$·mol$^{-2}$ | $\gamma_1$/N·m$^{-1}$ | RMSE/N·m$^{-1}$ |
|---|---|---|---|---|---|---|
| HTABr | 1.235 | 6.4141 | -5.0880 | 1.4855 | $5.7425 \times 10^{-2}$ | $4.4954 \times 10^{-4}$ |
| OTABr | 4.859 | 6.8382 | -15.835 | 12.254 | $7.4993 \times 10^{-2}$ | $4.0170 \times 10^{-4}$ |
| DTABr | 17.692 | 6.9150 | -72.384 | 245.78 | $6.6672 \times 10^{-2}$ | $7.2229 \times 10^{-4}$ |

Density functional theory B3LYP [4] with the basis set Def2-TZVP [5,6] has been exploited to optimize the geometry structures of HTABr, OTABr and DTABr. Their molecular sizes are then calculated and plotted with Multiwfn.[7] Since three surfactants are the alkyl-trimethylammonium bromide family but with different alkyl length, only OTABr is shown in Fig. S1.

Besides density functional theory calculation, MP2 [8] calculations have also been carried out to estimate the molecular areas of surfactants. The lengths of HTABr, OTABr and DTABr are 12.95, 15.50 and 18.04 Å, respectively. The smallest and biggest molecular areas estimated from MP2 calculations are 34.14 and 60.12 $\text{Å}^2$ separately. These calculations confirm the results of density functional theory.
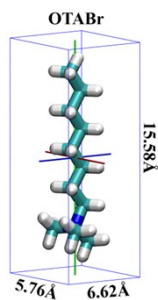
Figure S1. Molecular size of OTABr without bromide ion

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