Supporting Information

Evaluation of Ion Effects on Surfactant Aggregation from Improved Molecular Thermodynamic Modeling

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Model Derivation

Assuming the monomeric surfactant m_i (i=1, 2, or 3...) is completely dissociated in aqueous solution containing counterion m_j (j=1, 2, or 3…) but in the micelle form the surfactant is associated to some extent with counterions, therefore, the surfactant micellization is described by the following process [1-2]

$$n \sum_i \alpha_i m_i{}^{z_i} + n \sum_j \delta_j m_j{}^{z_j} \leftrightarrow M_{n\alpha_i\delta_j}^{n(\sum_i \alpha_i z_i + \sum_j \delta_j z_j)} \tag{1}$$

where α_i is the composition of surfactant i in the micelle, $M_{n\alpha_i\delta_j}$, which has an micelle size n, micelle composition α_i, and a counterion binding coefficient δ_j [3]. For micelles of pure surfactant, $\alpha_i = 1$; for mixed micelles, $0 < \alpha_i < 1$. z_i and z_j are the valences of ionic surfactant i in dissociated form and counterion j. For nonionic surfactant i, $z_i = 0$ and $\delta_j = 0$.

By the consideration of activity coefficient [1, 4], the chemical potential of micelle $M_{n\alpha_i\delta_j}$, monomeric surfactant i, and counterion j in solution can be written, respectively, as

$$\mu_{n\alpha_i\delta_j} = \mu_{n\alpha_i\delta_j}^o + kT\ln(a_{n\alpha_i\delta_j}) = \mu_{n\alpha_i\delta_j}^o + kT\ln(\gamma_{n\alpha_i\delta_j} X_{n\alpha_i\delta_j}) \tag{2}$$

$$\mu_{mi} = \mu_{mi}^o + kT\ln(a_{mi}) = \mu_{mi}^o + kT\ln(\gamma_{mi} X_{mi}) \tag{3}$$

$$\mu_{mj} = \mu_{mj}^o + kT\ln(a_{mj}) = \mu_{mj}^o + kT\ln(\gamma_{mj} X_{mj}) \tag{4}$$

where $\mu_{n\alpha_i\delta_j}{}^o$, $\mu_{mi}{}^o$ and $\mu_{mj}{}^o$ are the standard chemical potentials of micelle, monomeric surfactant, and counterion in solution, respectively. The standard state of water is defined as pure liquid while the standard state of all other species is defined for an infinitely dilute solution. $a_{n\alpha_i\delta_j}$, a_{mi}, and a_{mj} are the corresponding activities. $\gamma_{n\alpha_i\delta_j}$, γ_{mi}, and γ_{mj} are the corresponding activity coefficients. Micelle is treated as one separate phase from aqueous solution and thus $\gamma_{n\alpha_i\delta_j} = 1$. $X_{n\alpha_i\delta_j}$, X_{mi}, and X_{mj} are mole fractions of micelle, monomeric surfactant, and counterion in bulk solution.

Assume the activity coefficient of ionic surfactant i, γ_{mi}, in bulk solution is given by the quadratic mean of the product of functional headgroup activity coefficient γ_{hmi} and hydrocarbon tail activity coefficient γ_{tmi}. γ_{hmi} can be calculated from Pitzer's method [5]. γ_{tmi} is estimated from the Setchenov equation [6] shown as below

$$\gamma_{mi} = \sqrt{\gamma_{hmi}\gamma_{tmi}} \tag{5}$$

$$\gamma_{tmi} = 10^{I \sum_s \alpha_s k_s} \tag{6}$$

where I is ionic strength of solution. k_s and α_s are Setchenov coefficient and mole fraction of salt s in total added salts, respectively. k_s is salt-dependent and therefore salts with one ion in common should have different k_s. It is expected that the effect of counterion and coion on aggregation properties might be reflected through k_s. $\alpha_s = 1$ for pure salt added to solution; $0 < \alpha_s < 1$ if more than one type of salt is added. Note that the activity coefficient of nonionic surfactant is assumed as γ_{tmi}.

At equilibrium

$$\mu_{n\alpha_i\delta_j} = n\sum_i \alpha_i\mu_{mi} + n\sum_j \delta_j\mu_{mj} \tag{7}$$

$$\mu^o_{n\alpha_i\delta_j} + kT\ln(X_{n\alpha_i\delta_j}) = n\sum_i \alpha_i(\mu^o_{mi} + kT\ln(\gamma_{mi}X_{mi})) + n\sum_j \delta_{mj}(\mu^o_{mj} + kT\ln(\gamma_{mj}X_{mj})) \tag{8}$$

Standard micellization free energy per surfactant molecule is given by

$$\Delta\mu^o_{mic} = \frac{1}{n}\mu^o_{n\alpha_i\delta_j} - \sum_i \alpha_i\mu^o_{mi} - \sum_j \delta_j\mu^o_{mj} \tag{9}$$

Substitution of Eq. (9) into Eq. (8) leads to

$$\Delta\mu^o_{mic} = kT\sum_i \alpha_i\ln(\gamma_{mi}X_{mi}) + kT\sum_j \delta_j\ln(\gamma_{mj}X_{mj}) - \frac{kT}{n}\ln X_{n\alpha_i\delta_j} \tag{10}$$

Rearrangement of Eq. (10) leads to

$$X_{n\alpha_i\delta_j} = \prod_i(\gamma_{mi}X_{mi})^{n\alpha_i} \prod_j(\gamma_{mj}X_{mj})^{n\delta_j} \exp\left(-\frac{n}{kT}\Delta\mu^o_{mic}\right) \tag{11}$$

Further rearrangement leads to

$$X_{n\alpha_i\delta_j} = \prod_i(X_{mi})^{n\alpha_i} \prod_j(X_{mj})^{n\delta_j} \exp\left(-\frac{n}{kT}\left(\Delta\mu^o_{mic} + kT\ln\left(\prod_i(\gamma_{mi})^{-\alpha_i} \prod_j(\gamma_{mj})^{-\delta_j}\right)\right)\right) \tag{12}$$

Here X_{mi} is the mole fraction of monomeric surfactant i in bulk solution and is equal to

$$X_{mi} = x_{mi}\sum_i X_{mi} \tag{13}$$

where x_{mi} is interpreted as the mole fraction of surfactant i in the total mixed surfactants. X_m is the total mole fraction of monomeric surfactants in bulk solution. Only monomeric surfactants are taken into account in Eq. (13) considering that the mole fraction of micelles is negligible compared to that of monomers.

Eq. (12) is simplified to

$$X_{n\alpha_i\delta_j} = \prod_i(X_{mi})^{n\alpha_i} \prod_j(X_{mj})^{n\delta_j} \exp\left(-\frac{n}{kT}\Delta\mu^o_m\right) \tag{14}$$

where $\Delta\mu_m^o$ is the modified standard micellization free energy by the consideration of surfactant and ion activities and estimated by summing the contributing terms as described below

$$\Delta\mu^o_m = \Delta\mu^o_{trt} + \Delta\mu^o_{int} + \Delta\mu^o_{pack} + \Delta\mu^o_{st} + \Delta\mu^o_{ent} + \Delta\mu^o_{elec} + \Delta\mu^o_{act} \tag{15}$$

Where $\Delta\mu_{trt}^o$, $\Delta\mu_{int}^o$, $\Delta\mu_{pack}^o$, $\Delta\mu_{st}^o$, $\Delta\mu_{ent}^o$, and $\Delta\mu_{elec}^o$ are the standard free energy contributions from hydrocarbon transfer from water into micelle, formation of micellar core-water interface, hydrocarbon tail packing in the micelle, surfactant headgroup steric interaction, headgroup-counterion mixing, and electrostatic interaction, respectively [7-12]. $\Delta\mu_{act}^o$ comes from the activity contribution.

Hydrocarbon tail transfer contribution $\Delta\mu_{trt}^o$

$\Delta\mu_{trt}^o$ consists of two parts: (a) the hydrocarbon tail transfer from aqueous solution containing salts to pure water $\Delta\mu_{tr,s/w}^o$; (b) the subsequent transfer from pure water to the micellar core $\Delta\mu_{tr,w/mic}^o$. Details for these events and free energies can be found in literature [7, 13]. The Setchenov coefficient k_s for the calculation of $\Delta\mu_{tr,s/w}^o$ is per CH_2 group based, which is different from the hydrocarbon tail volume-based k_s [14]. Considering the CH_2 group adjacent to headgroup possess weaker hydrophobicity than the CH_2 groups away from headgroup and that the CH_3 group at the

end of the tail may have stronger hydrophobicity, k_s multiplied by tail length should give a reasonable estimation of the salt effect on the entire hydrocarbon tail transfer.

Micellar core-water interface formation contribution $\Delta\mu_{\text{int}}^{\text{o}}$

The interfacial free energy contribution is calculated by the equation [7, 9-10]

$$\frac{\Delta\mu_{\text{int}}^{\text{o}}}{kT} = \sum_i \alpha_i \sigma_{\text{int},i}(a - a_{\text{oi}}) \tag{16}$$

where a is the area per surfactant molecule i at micellar core-water interface; a_{oi} is the area per surfactant molecule i at the interface shielded by the headgroup. $a_{\text{oi}} = \min(L^2, a_{\text{hi}})$. L is the characteristic methylene segment length of the tail ($L=0.46$ nm), and a_{hi} is the effective cross-sectional area of the hydrated headgroup of surfactant i.

$$a = \frac{S\sum_i \alpha_i v_{\text{ti}}}{l_c} \tag{17}$$

$$a_{\text{hi}} = \sum_j \frac{C_j}{\sum_j C_j} a_{ij} \tag{18}$$

S is shape factor: $S=3$ for sphere; $S=2$ for cylinder; $S=1$ for disk. v_{ti} is the hydrocarbon tail volume of surfactant i. l_c is micellar core minor radius. C_j is molar fraction of counterion j in total counterions. a_{ij} is the effective cross-sectional area of the headgroup of surfactant i associated with counterion j for surfactants [12]. The cross-sectional area of Octylglucoside (OG) and polyoxythylene (C_nE_n) are comparable to the reported values [15].

In Eq. (16) $\sigma_{\text{int},i}$ is the interfacial tension between water and surfactant i in micelle phase and is given by [16-17]

$$\sigma_{\text{int},i} = 0.7562\left(\sigma_{\text{sur},i} + \sum_s \alpha_s \sigma_s\right) - 0.4906\left(\sigma_{\text{sur},i} \sum_s \alpha_s \sigma_s\right)^{0.5} \tag{19}$$

$$\sigma_{\text{sur},i} = 29.7003[1 - \exp(-0.1532n_i)] - 0.0896(T - 298.15) \tag{20}$$

$$\sigma_s = \sigma_w + \left(\frac{d\sigma_o}{dC_s}\right)C_s \tag{21}$$

$$\sigma_w = 235.8(1 - \frac{T}{647.15})^{1.256}\left[1 - 0.625(1 - \frac{T}{647.15})\right] \tag{22}$$

Where $\sigma_{\text{sur},i}$ is the surface tension of normal alkane tails from surfactant i[18]. σ_s is the surface tension of aqueous solution with added salt [19]. σ_w is the surface tension of pure water [20]. n_i is the hydrocarbon chain length of surfactant i. T is the absolute temperature. C_s is the salt concentration in unit M. $(d\sigma_o/dC_s)$ is the correlation between surface tension and salt concentration [21]. Setchenov coefficients of different salts can be found elsewhere [13].

Hydrocarbon tail packing contribution $\Delta\mu_{\text{pack}}^{\text{o}}$

The packing free energy arises from the constraint of one end of surfactant tail at the micelle core-water interface, while the entire tail assumes a uniform conformation in the micelle core. Calculation of packing free energy of pure surfactant directly followed the method proposed by R. Nagarajan [22]. For mixed surfactants, an averaged-number of segments in the tail was used based on mixed composition.

Headgroup steric interaction $\Delta\mu_{\text{st}}^{\text{o}}$

The steric free energy considers the interaction between headgroups and counterions at the micellar core-water interface based on the assumption that the surfactants and counterions are components of an ideal monolayer at the interface [23]. Details of calculation can be found elsewhere [7, 23]. The radius of hydrated counterions is summarized elsewhere in [15, 23]. These values are very close to reported results [15].

Headgroup-counterion mixing entropy $\Delta\mu_{\text{ent}}^{\text{o}}$

The free energy contribution accounts for the entropy gain associated with the mixing of surfactant components and counterions and is modeled by ideal mixing in which all the components are randomly distributed on the micelle surface [23].

Electrostatic contribution $\Delta\mu_{elec}{}^o$

The electrostatic free energy contribution arises from the building of an electrical double layer around micelles and is evaluated for spherical and cylindrical micelle respectively by

$$\frac{\Delta\mu_{elec}^o}{kT} = \frac{2\pi q^2 d_{st}}{a\epsilon\left(1+\frac{d_{st}}{l_c}\right)} + \frac{a_{ch}\kappa}{4\pi\lambda_B}\int_0^t \varphi(x_o)\, dt \tag{23}$$

$$\frac{\Delta\mu_{elec}^o}{kT} = \frac{2\pi q^2 l_c}{a\epsilon}\ln\left(1+\frac{d_{st}}{l_c}\right) + \frac{a_{ch}\kappa}{4\pi\lambda_B}\int_0^t \varphi(x_o)\, dt \tag{24}$$

The first term on the right side of Eq. (23) and Eq. (24) represent the contribution from Stern layer; the 2nd term represents electrostatic interaction between micelle and ions. d_{st} is the thickness of the Stern layer and is estimated from the structure of hydrated headgroup and hydrated counterion. The value of d_{st} used in the present model is either estimated from surfactant structure or adopted from MF model [7]. a_{ch} is the area per surfactant molecule at the micelle surface of charge. κ is the inversed Debye length. λ_B is the Bjerrum length. t is a function of micelle surface charge density σ. $\varphi(x_o)$ is the surface electrical potential at the micelle surface of charge. These parameters are described below.

$$a_{ch} \approx \frac{S(v_t+v_h)}{r_{ch}} \tag{25}$$

$$r_{ch} = d_{ch} + l_c \tag{26}$$

$$v_t = \sum_i \alpha_i v_{ti} \tag{27}$$

$$v_h = \sum_i \alpha_i v_{hi} \tag{28}$$

$$v_{hi} \approx \frac{4\pi\left(\frac{a_{ij}}{\pi}\right)^{3/2}}{3} \tag{29}$$

$$\kappa = \left(\frac{2e^2 I}{\epsilon\epsilon_o kT}\right)^{1/2} \tag{30}$$

$$\epsilon = \epsilon_w + \sum_s \delta_s \alpha_s C_s \tag{31}$$

$$\epsilon_w = -1.0677 + 306.4670\exp(-4.52\times10^{-3}T) \tag{32}$$

$$\lambda_B = \frac{e^2}{4\pi\epsilon\epsilon_o kT} \tag{33}$$

$$t = \frac{4\pi\sigma\lambda_B}{e\kappa} \tag{34}$$

$$\sigma = \frac{e(\sum_i \alpha_i z_i + \sum_j z_j \delta_j)}{a_{ch}} \tag{35}$$

where v_t is the average volume of hydrocarbon tails. v_h is the average volume of hydrated headgroups associated with counterions. r_{ch} is the radius of the micelle surface of charge. The electrostatic contribution barely changes with and without v_h in Eq. (25). v_{hi} is the volume of headgroup of surfactant i. d_{ch} is the distance from the surface of micellar core to the center of charged headgroup. Therefore d_{ch} is zero for nonionic surfactant. For mixture d_{ch} is the average value based on mixed composition. The schematic representation of interfacial region with d_{ch} and d_{st} can be

found elsewhere [7, 15]. e is the elementary positive charge. I is ionic strength. ϵ, ϵ_w, and ϵ_o are the dielectric constant of solvent, water, and vacuum, respectively [24-25]. δ_s is the dielectric decrement of added salt [26]. δ_s is salt-dependent and therefore salts with one ion in common should have different δ_s. It is expected that the effect of coion on aggregation properties might be reflected through δ_s. It is actually expected that all salt-dependent factors may exhibit the coion effects on aggregation properties.

To calculate the integration in Eq. (23) and Eq. (24), the linearized PB equation is solved with respect to surface potential $\varphi(x_o)$. Because the linearized PB equation can only be numerically solved for one-dimensional problem, the analytical solution of surface potential from PB equation of two- and three-dimensional problems are more interested in. Following the method reported by Andreev and Victorov [8], three-dimensional problems are reduced to an effective one-dimensional problem by the introduction of an angle-averaged Laplacian operator. An effective generalized one-dimensional form of PB equation for spherical, cylindrical, and planar geometries is given by

$$\frac{d^2\varphi}{dx^2} + \left(\frac{S-1}{x}\right)\frac{d\varphi}{dx} = u \tag{36}$$

with the boundary conditions of

$$\frac{d\varphi}{dx}\Big|_{x=\infty} = 0 \tag{37}$$

and

$$\frac{d\varphi}{dx}\Big|_{x=x_o} = -t \tag{38}$$

The solution of Eq. (33) is given by

$$\varphi(x) = \frac{e\sigma}{\varepsilon\epsilon_o\kappa kT}\left(\frac{x_o}{x}\right)^\upsilon \frac{K_\upsilon(x)}{K_{\upsilon+1}(x_o)} \tag{39}$$

where $K_v(x)$ is modified Bessel function of the second kind and $v=(S-2)/2$. Given the values of v and x, $K_v(x)$ can be estimated [27].

Substitution of $\varphi(x)$ at $x=x_o$ into the Eq. (23) and Eq. (24) leads to

$$\frac{\Delta\mu_{elec}^o}{kT} = \frac{a_{ch}\kappa}{8\pi\lambda_B}\frac{K_\upsilon(x_o)}{K_{\upsilon+1}(x_o)}t^2 \tag{40}$$

with

$$x_o = r_{ch}\kappa \tag{41}$$

Activity coefficient contribution $\Delta\mu_{act}{}^o$

The activity coefficient contribution comes from the incorporation of activity coefficient term into exponential part in Eq. (11) and is given by

$$\frac{\Delta\mu_{act}^o}{kT} = \ln\left(\prod_i(\gamma_{mi})^{-\alpha_i}\prod_j(\gamma_{mj})^{-\delta_j}\right) \tag{42}$$

Free Energy Minimization and Parameter Determination

The standard micellization free energy $\Delta\mu_m^o(S, \alpha_i, l_c, \delta_j)$ depends on micelle shape S, micelle composition α_i, micellar core minor radius l_c, and counterion binding coefficient δ_j, at given solution conditions (model inputs) which include the composition of surfactant i in total mixed surfactants in bulk solution, x_{mi}, temperature T, salt or mixed salts concentration C_s. In the present research the minimization of $\Delta\mu_m^o(S, \alpha_i, l_c, \delta_j)$ is only performed for spherical micelles ($S=3$), and infinite cylindrical micelles ($S=2$) respectively, with respect to independent variables S,

α_i, l_c, and δ_j under the constraints of $0<\alpha_i<1$ (for pure surfactant $\alpha_i = 1$), $0<l_c<l_o$ (l_o is the longest extended chain length among all the surfactants i), and $0<\delta_j<1$. The minimization is calculated using MATLAB program, which is a process of multiple-variable (S, α_i, l_c, and δ_j) non-linear optimization.

The required model inputs are solution conditions, surfactant structural properties, salt-associated empirical parameters, and ion radius. The outputs include a set of optimized variables S, α_i, l_c, and δ_j, the minimized micellization free energy $\Delta\mu_m{}^o$, cmc, micelle size, and sphere-to-rod transition.

If the standard micellization free energy of spherical micelle is minimum, optimized shape should be sphere ($S=3$). The cmc is assumed to be equal to monomer concentration $X_{m, sph}$ (here this is the mole fraction) and is calculated by

$$X_{cmc,sph} = \exp\left(\frac{1}{kT}\Delta\mu_{m,sph}^o\right) \tag{43}$$

The micelle size distribution is assumed to be monodisperse and is given by

$$X_{n\alpha_i\delta_j,sph} = \frac{X - X_{cmc,sph}}{n_{sph}} \tag{44}$$

The micelle size given by [28]

$$n_{sph} = \frac{\frac{4}{3}\pi(l_{c,sph})^3}{v_{t,sph}} \tag{45}$$

If the standard micellization free energy of cylindrical micelle is minimum, the optimized shape should be a cylinder ($S=2$). The mass balance equations (46)-(48) as well as Eq. (14) need to be solved simultaneously with respect to X_m, X_{mi}, and X_{mj}:

$$X = X_m + \sum_{n=n_{sph}}^{\infty} nX_{n\alpha_i\delta_j} \tag{46}$$

$$X_i = X_{mi} + \sum_{n=n_{sph}}^{\infty} n\alpha_i X_{n\alpha_i\delta_j} \tag{47}$$

$$X_j = X_{mj} + \sum_{n=n_{sph}}^{\infty} n\delta_j X_{n\alpha_i\delta_j} \tag{48}$$

The ladder model [29-30] is used to solve the micelle size distribution in terms of a finite cylindrical micelle.

With the determined X_m, X_{mi}, and X_{mj} micelle size distribution can be completely evaluated using Eq. (14). Weight-based micelle size are calculated as follows [31]

$$n_n = \frac{M_1}{M_0} \tag{49}$$

$$n_w = \frac{M_2}{M_1} \tag{50}$$

$$n_z = \frac{M_3}{M_2} \tag{51}$$

where n_n, n_w, and n_z are the number-based, weight-based, and z-based micelle size, respectively. M_k ($k = 1, 2, or 3$) is defined as

$$M_k = \sum_{n=n_{sph}}^{\infty} n^k X_{n\alpha_i\delta_j} \tag{52}$$

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