**Surfactants and Micelles: Non-Ionics**

The properties of aqueous solutions containing non-ionic surfactants [1-6] can be described using two models.

**Model Phase Equilibrium: Dry Micelle**

We envisage a non-ionic surfactant $X$. When chemical substance $X$ is added to $n_1$ moles of water (at fixed $T$ and $p$), solute $X$ exists as a simple solute $X_{\text{aq}}$ until the concentration of solute $X$, $c_X$ reaches a characteristic concentration $c_{\text{mc}}$ when a trace amount of the micellar phase appears. Each micelle comprises $n$ molecules of surfactant $X$. The equilibrium between monomer surfactant $X_{\text{aq}}$ and surfactant in the micelles is described by the following equation.

\[
\mu_{X_{\text{aq}}}^\text{eq} = \mu_{X_{\text{mic}}}^*(a) \tag{a}
\]

If $X_{\text{aq}}$ is a typical neutral solute in aqueous solution $\mu_{X_{\text{aq}}}^\text{eq}$ is related to the $c_{\text{mc}}$ of $X_{\text{aq}}$ in solution at the point where only a trace amount of micellar phase exists.

Hence,

\[
\mu_{X_{\text{aq}}}^0(c - \text{scale}) + R \cdot T \cdot \ln(c_{\text{mc}} \cdot y_X / c_r) = \mu_{X_{\text{mic}}}^*(a) \tag{b}
\]

Here $y_X$ is the solute activity coefficient for $X_{\text{aq}}$ taking account of solute-solute interactions in the aqueous solution. Therefore, by definition,

\[
\Delta_{\text{mic}} G^0(aq) = -R \cdot T \cdot \ln(K_{\text{mic}}^0) = \mu_{X_{\text{mic}}}^*(a) - \mu_{X_{\text{aq}}}^0(c - \text{scale}) \tag{c}
\]

Equilibrium constant $K_{\text{mic}}^0$ describes the phase equilibrium involving surfactant $X$ in aqueous solution and micellar phase.

\[
\Delta_{\text{mic}} G^0(aq) = -R \cdot T \cdot \ln(K_{\text{mic}}^0) = R \cdot T \cdot \ln(c_{\text{mc}} \cdot y_X / c_r) \tag{d}
\]

If $X_{\text{aq}}$ is a neutral solute and the $c_{\text{mc}}$ is low, a useful approximation sets $y_X$ at unity. Therefore $\Delta_{\text{mic}} G^0(aq)$ is the standard increase in Gibbs energy when one mole of surfactant $X_{\text{aq}}$ forms one mole of $X$ in the micellar phase. Combination of equations (c) and (d) yields equation (e).

\[
K_{\text{mic}}^0 = (c_{\text{mc}} / c_r)^{-1} \tag{e}
\]

Here $K_{\text{mic}}^0$ describes the equilibrium between surfactant in the micellar phase and the aqueous solution. A famous equation suggested by Harkin
relates the cmc to the number of carbon atoms in the alkyl chain, nC; equation (f)
\[
\log(\text{cmc} / c_r) = A - B \cdot n_C \quad (f)
\]

With equation (e), \( \log(K_{\text{mic}}^0) = A - (B \cdot n_C) \quad (g) \)

The above analysis is also used for ionic surfactants if it can be assumed the degree of counter ion binding by the micelles is small, the thermodynamic properties of the solution are ideal and the aggregation number is high.

**Non-Ionic Surfactant: Phase Equilibrium: Wet Micelle** The aqueous phase comprises an aqueous solution of solute X, X(aq). The micellar phase comprises both water and surfactant X such that the mole fraction of surfactant in the micellar phase equals \( x_X^{eq} \). We treat the micellar phase using the procedures used to describe the properties of a binary liquid mixture. For the micellar phase the chemical potential of X is given by the following equation.
\[
\mu_X^{\text{mic}} = \mu_X^{*}(\text{mic}) + R \cdot T \cdot \ln(x_X \cdot f_X)^{eq} \quad (h)
\]

where \( \lim(x_X \to 1)f_X = 1 \) at all T and p \( (i) \)

But at equilibrium for a system containing a trace of the micellar phase, \( \mu_X^{eq}(\text{mic}) = \mu_X^{eq}(\text{aq}) \quad (j) \)

Then, \( \mu_X^{*}(\text{mic}) + R \cdot T \cdot \ln(x_X \cdot f_X)^{eq} = \mu_X^{eq}(\text{aq}) + R \cdot T \cdot \ln(\text{cmc} \cdot y_X / c_r) \quad (k) \)

By definition \( \Delta_{\text{mic}}G^0 = -R \cdot T \cdot \ln(K_{\text{mic}}^0) = \mu_X^{*}(\text{mic}) - \mu_X^{eq}(\text{aq}) \quad (l) \)

Then, \( K_{\text{mic}}^0 = [x_X \cdot f_X]^{eq} / [\text{cmc} / c_r] \quad (m) \)

If the micelle is only ‘damp’ rather than wet, a reasonable assumption sets \( f_X \) equal to unity although it is not obvious how \( x_X \) might be determined.

**Non-Ionic Surfactant: Mass Action Model: Dry Micelle**

Micelle formation is described as an equilibrium between X(aq) as a solute in aqueous solution and a micellar aggregate in aqueous solution
formed by $n$ molecules of the monomer $X(aq)$. Then at the point where micelles are first formed, the following equilibrium is established.

$$nX(aq) \rightleftharpoons X_n(aq)$$  (n)

The total amount of surfactant in the system equals $N(X;aq) + n \cdot N(X_n;mic)$ where $N(X;aq)$ is the amount of monomer surfactant and where $N(X_n;mic)$ is the total amount of micelles, each micelle containing $n$ surfactant molecules.

But for the micellar aggregate $X_n(aq)$ treated as a single solute,

$$\mu(X_n;aq) = \mu^0(X_n;aq) + R \cdot T \cdot \ln [c(X_n) \cdot y(X_n) / c_r]$$  (o)

Here $c(X_n) [= N(X_n;aq)/V$ where $V$ is the volume of the system] is the concentration of micelles in the system, activity coefficient $y(X_n)$. The latter can be assumed to be unity if there are no micelle-micelle interactions and no micelle-monomer interactions in the aqueous system. Although this approach seems similar to that used to describe chemical equilibria, the procedure has problems in the context of determining $c(X_n)$.

**Footnotes**


