New Interpretation of Small System Thermodynamics Applied to Ionic Micelles in Solution and Corrin-Harkins Equation

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Abstract: Surfactant micelle should typically be regarded as a small system characterized by non linear homogeneity of the thermodynamic functions. Aqueous micellar solutions of single component ionic surfactant with an electrolyte added have been treated by the small system thermodynamics. The functional form of chemical potential \( \mu_M \) of interacting micelles in solution has been determined. The aggregation number distribution and the mean degree of counterion binding \( \beta \) of ionic micelles are discussed in detail, in which the condition to make \( \beta \) constant at given \( T \) and \( P \) is obtained. Corrin-Harkins equation and its linearity have theoretically been discussed in relation to the definitions of critical micelle concentration. The gradient of linear Corrin-Harkins plot can to good approximation presume the value of \( \beta \) of micelles in solutions at concentrations higher than CMC as well as at CMC.

Key words: aggregation number distribution, Corrin-Harkins equation, degree of counterion binding, ionic micelles, Gibbs-Duhem type equation, small system thermodynamics

1 Introduction

Micellar solution of surfactant is treated as an ensemble of completely open micellar small systems dispersed in monomeric solution. Small system thermodynamics (1,2) should give the following equation of Gibbs-Duhem type to an ensemble of \( NM \) micellar small systems of c components in solution (see Appendix 3).

\[
0 = -S_d dT + V_d dP - \sum_{i=1}^{c} N'_i d\mu'_i - N_M d\mu_M + \sum_{i=1}^{c} \mu_i N_M dN_i \quad [1a]
\]

where

\[
\mu_M = \sum_{i=1}^{c} N_i \mu_i^0 + \epsilon \quad [1b]
\]

\( N'_i \) and \( N_i \) are the number of monomeric species i in the free solution and the mean aggregation number of monomeric species i per micelle. \( \mu'_i \) and \( \mu_i^0 \) are respectively the chemical potentials of species i in free solution (s) and in micellar state (m). \( \mu_M \) is the mean chemical potential of micellar small system (M) in solution, \( \epsilon \) being the subdivision potential of micelles. Micellar solutions are regarded as being in complete equilibrium (3) in which holds \( \epsilon = 0 \) as well as \( \mu'_i = \mu_i^0 = \mu_i \).

If we have polydispersed micelles as characterized by the numbers \( N_r (=y_r N_M) \) of the rth micellar species \( M_r \) containing \( N'_r \) of monomeric i, eqs. [1a, b] are rewritten to

\[
0 = -S_d dT + V_d dP - \sum_{r} N'_r d\mu'_r - \sum_r N_r d\mu_r \quad [2a]
\]

\[
\mu_r = \sum_r N'_r \mu_r^0 + \epsilon \quad [2b]
\]

where \( \mu_r \) is the chemical potential of \( M_r \). We have here

\[
\mu_M = \sum_r y_r \mu_r \quad [3]
\]

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where \( y_i = N_i / N \) and \( \sum_i N_i = N_M \).

The aim of the present paper is to reexamine and reinterpret the application of small system thermodynamics to surfactant micelles in solution (1-3) by the use of eq. [1] and eq. [2].

Hill (1) pointed out that the small system thermodynamics cannot be applied to the ensemble of small systems which interact significantly with each other. Hall and Pethica (2) applied the small system thermodynamics to an ensemble of \( N_M \) non-interacting multi-component nonionic micellar small systems in solution. It should be noted that there are some ambiguities left in their theories, for instance, in the expression of \( \mu_M \). Hall and Pethica (2) expressed \( \mu_M \) of noninteracting micelles as

\[
\mu_M = \overline{G}(T, P, \overline{N}_i, N'_i) + kT \ln x_M
\]

[4]

where \( \overline{G}(T, P, \overline{N}_i, N'_i) \) is the mean reference Gibbs free energy of micelles, and \( x_M = N_M / (\sum_i N'_i + N_M) \).

Hill (1) used the same form of equation as eq. [4], in which are used \( \overline{G} = \overline{G}(T, P, \overline{N}_i, sc) \) and \( x'_M = N_M / (\sum_i N'_i) \) in stead of \( x_M \), where \( sc \) denotes solvent composition.

It seems problematic to regard the reference free energy \( \overline{G} \) as being an explicit function of \( N'_i \) or \( sc \) as well as \( T, P \) and \( \overline{N}_i \). This only serves to make things complicated. After having done complicated and ambiguous discussions, Hall and Pethica (2) came to make an approximation that \( \overline{G} = \overline{G}(T, P, N) \). It should be stressed here that such ambiguity about the reference free energy can completely be removed by the Gibbs-Duhem type equations [1a] and [2a] being applied.

It is reasonable to assume Raoult’s law holds for solvent water 1 and Henry’s law for monomeric solute species \( i (\neq 1) \) in solution of noninteracting micelles (4). Chemical potentials \( \mu'_i \) and \( \mu_i \) of solvent water 1 and monomeric solute \( i \) in solution are written as

\[
\mu'_i = \mu_i(T, P) + kT \ln x'_i
\]

[5a]

\[
\mu_i = \mu_i(T, P) + kT \ln x_i
\]

[5b]

where \( x'_i = N'_i / (\sum_i N'_i + N_M) \). Substituting eqs.[5a] and [5b] in eq. [1a] at given \( T \) and \( P \), and using an identical equation \( 0 = \sum_i x'_i \ln x'_i + x_M d \ln x_M \), we obtain

\[
[d(\mu_M - kT \ln x_M)]_{T, P} = \sum_i \mu_i d \overline{N}_i
\]

which shows that \( (\mu_M - kT \ln x_M) \) should be a function of \( T, P \) and \( \overline{N}_i \). Let the function be \( \overline{G}(T, P, \overline{N}_i) \). We obtain the following form of equation for \( \mu_M \) in stead of eq. [4]

\[
\mu_M = \overline{G}(T, P, \overline{N}_i) + kT \ln x_M
\]

[6]

and obtain the equation for \( G = \overline{G}(T, P, \overline{N}_i) \) to obey

\[
d\overline{G}(T, P, \overline{N}_i) = -\overline{s}dT + \overline{\nabla}dP + \sum \mu_i d \overline{N}_i
\]

[7]

where are used \( \mu'_i = \mu_i = \mu \) at equilibrium. Substituting eqs. [5a, b] for \( \mu'_i \) in eq. [2a] and using \( 0 = \sum_i x'_i \ln x'_i + \sum_i x_i \ln x_i \); \( x_i = N_i / (\sum_i N'_i + N) \), we obtain for \( \mu \)

\[
\mu_i = G_i(T, P) + kT \ln x_i
\]

[8]

It should be noted here that we can not find any evidence for eqs. [1a] and [2a] to be restricted to ideal solutions of non-interacting small systems. It is possible to use eqs. [1a] and [2a] in order to know thermodynamically reasonable functional forms of \( \mu_M \) and \( \mu_i \) of interacting micellar small systems in solution.

According to the intuition coming from the macroscopic solution thermodynamics, it seems useful to reinterpret the application of small system thermodynamics, it seems useful to express \( \mu'_i \), \( \mu_M \) and \( \mu_i \) in solutions of interacting micelles mathematically in the same form as ideal equations [5a], [5b], [6] and [8] in which the mole fractions are simply replaced by the activities as the followings.

\[
a'_i = x'_i \gamma'_i \quad a_M = x_M \gamma_M \quad a_i = x_i \gamma_i
\]

[9a, b, c]

where \( \gamma_i, \gamma_M, \gamma_i \to 1 \) as \( x'_i \to 1 \). Here it is indispensable to examine the validity of such intuitive expressions of \( \mu'_i \), \( \mu_M \) and \( \mu_i \) of interacting micellar small systems in solution by the use of eqs.[1a] and [2a].

Hall (5) has derived the following equations for interacting nonionic micelles without reference to eqs.[1a] and [2a].

\[
d\overline{G} = -\overline{s}dT + \overline{\nabla}dP + \sum \mu_i d \overline{N}_i - kT \sum \ln \gamma_i dy_i
\]

[10]

\[
d(kT \ln a_M) = -\overline{s}dT + \overline{\nabla}dP - \sum \overline{N}_i d \mu_i - kT \sum \ln \gamma_i dy_i
\]

[11]

After complicated discussion, Hall (5, 7) made an assumption that

\[
\sum \ln \gamma_i dy_i = 0
\]

[12]

It is obvious that eq. [12] should hold if all micellar species \( M \), have the same activity coefficient, i.e. \( \gamma_i = \gamma_M \) for all \( r \). Hall pointed out that \( \gamma_i = \gamma_M \) is most likely to be valid for micelles which approach monodispersity with respect to size and composition.

The properties of activity coefficients \( \gamma'_i, \gamma_M \) and \( \gamma_i \),
should generally be determined so as to be compatible with the property of \( G \) of the reference state chosen. It is reasonably possible to take the reference free energy \( G \) so as to obey an equation of the same form as ideal equation [7] so that \( G = G(T, P, \bar{N}) \). This at once results in eq. [12] from eq. [10]. Then eq. [12] is not an assumption but a necessary condition for \( \eta \) to be compatible with \( G = G(T, P, \bar{N}) \). It can be seen from eq. [10] and eq. [12] being reexamined that \( \gamma_r = \gamma_m \) may hold for polydispersed micelles as well as for monodispersed ones.

Using eq. [12] in eq. [11] in any way, it is possible to apply the result to micellar solution of ionic surfactant \( D_{23} \) with an electrolyte \( X_{34} \) added, and to obtain the following equation.

\[
-d(kT \ln \alpha_m) = -SdT + \nabla dP - \bar{N}_3 \mu_r' - \bar{N}_3 \mu_m' \]  \[13\]

where is used \( \mu_r = \mu_r' \). It is reasonably assumed here as in ref. (7) that the presence of solvent water 1 can to good approximation be ignored in micelle formation, and the counterions 3 are either bound on the surfaces of micelles to neutralize much of surface charges of micelles formed from the aggregation of the surface active ions 2, or are free in solution, and non surface active simili-ions 4 are not present in micelles.

Using \( d\mu_r' = kT d \ln a_r' \) in eq. [13] at given \( T \) and \( P \), we obtain the following approximate equation

\[
d \ln a_r' = -\beta d \ln a_r' \]  \[14\]

where the ionic micelles are assumed to have sufficiently large \( \bar{N}_2 \) so that \( \bar{N}_2^{-1} d \ln \alpha_m \) may approximately be ignored. And \( \beta = \bar{N}_3 / \bar{N}_2 \) is defined as the mean degree of counterion binding of the ionic micelles. If \( \beta \) is constant at given \( T \) and \( P \), eq. [14] is integrated to

\[
\ln a_r' = -\beta \ln a_r' + I(T, P) \]  \[15\]

It should be stressed that linearity of eq. [15] has experimentally been verified in micellar solutions of various ionic surfactants (8-12). \( \beta = \beta(T, P) \) is an important clue to understand the behaviors of ionic micelles in solution. Small system thermodynamics can theoretically derive the condition that \( \beta = \beta(T, P) \) from the size distribution of micelles in solution.

Corrin-Harkins (C-H) equation (13) is an experimental equation just concerning the critical micelle concentration (CMC) suitably defined, which is written as the following (14).

\[
\ln(\text{CMC}) = -k_{CH} \ln[(\text{CMC}) + C_b] + b_{CH} \]  \[16\]

where \( C_b \) is the concentration of an added electrolyte, and \( C_r' = (\text{CMC}) + C_b \) is the total concentration of counterion 3 at \( C_r' = (\text{CMC}) \).

It is shown here the C-H equation [16] can approximately be derived from eq. [14] by the transformation of \( (a_r', a_m') \) to \( (C_r', C_m) \). And it is examined here in detail that if eq. [16] is experimentally found to be linear, the gradient \( k_{CH} \) is to assume the approximate value of \( \beta \) at concentrations higher than \( (\text{CMC}) \) as well as at \( (\text{CMC}) \).

It should be noted that the experimental \( (\text{CMC}) \) data can have sufficient arbitrariness so as to make Corrin-Harkins plot be linear.

Hall (3,15) applied Kirkwood-Buff statistical theory (16) together with the small system thermodynamics. Small system thermodynamics is based on the constitution of an ensemble of small systems, which is closely connected to the ensemble theory in statistical mechanics. So the small system thermodynamics can do considerable degree of presumption about the properties of small systems. It will be of large value to devotedly apply the small system thermodynamics to the ensemble of interacting ionic micelles in solution up to the limit of its applicability, without using any other statistical theories.

### 2 Theoretical

As mentioned above, intuition from macroscopic solution thermodynamics gives the following equations to non ideal \( \mu_r', \mu_m \) and \( \mu \),

\[
\mu_r' = \mu_r^i(T, P) + kT \ln \alpha_r' \]  \[17a\]

\[
\mu_m = \mu_m^i(T, P) + kT \ln \alpha_m \]  \[17b\]

\[
\mu_r = G_r(T, P) + kT \ln a_r \]  \[18\]

Eq. [19] is rewritten to as

\[
\mu_r = \mu_r^i + kT \ln a_r + kT \ln \eta_r ; \ \eta_r = \gamma_r / \gamma_m \]  \[20\]

where \( \mu_r^i \) is the new reference free energy defined as

\[
\mu_r^i(T, P, \eta_r) = G_r(T, P) + kT \ln \eta_r \]  \[21\]

From eq. [2b] and eq. [20], we obtain
Using eqs. [18] and [20] in eq. [3], we obtain

\[ \mu_i^v = \sum_{i=2}^3 N_i^v \mu_i^v + \varepsilon_m - kT \ln \eta_i \quad [22a] \]

\[ \varepsilon_m = \varepsilon - kT \ln a_m \quad [22b] \]

Using eqs. [18] and [20] in eq. [3], we obtain

\[ \mathcal{G}(T, P, \overline{N}_i) = \sum_r y_r \mu_r^v(T, P, y_r) \quad [23a] \]

\[ = \sum_r N_r \mu_r^v + \varepsilon_m \quad [23b] \]

where has been used.

\[ \sum_r y_r \ln \eta_r = 0 \text{ i.e. } \ln \gamma_M = \sum_r y_r \ln \gamma_r \quad [24a, b] \]

The reference entropies and volumes, \( \overline{S} \) and \( S_r^v \), and \( \overline{V} \) and \( V_r^v \) are related with each other as follows.

\[ \overline{S} = \sum_r y_r (S_r - k \ln y_r) = \sum_r y_r S_r^v(T, P, y_r) \quad [25a] \]

\[ \mathbf{V} = \sum_r y_r V_r^v = \sum_r y_r V_r^v \quad [25b] \]

where \( S_r = (\partial G_r / \partial T)_T \) and \( V_r = (\partial G_r / \partial P)_T \).

### 2.1 Reference Free Energy and Activity Coefficient

For an aqueous micellar solution of 1-1 ionic surfactant \( D_{23} \) with an electrolyte \( X_{34} \) added, eqs. [1a] and [2a] are rewritten as follows.

\[ 0 = -S_d T + V_d P - \sum_{i=1}^4 N_i^d \mu_i^d - N_M d \mu_M + \sum_{i=1}^4 \mu_i^v N_M d \overline{N}_i \quad [26] \]

\[ 0 = -S_d T + V_d P - \sum_{i=1}^4 N_i^d \mu_i^d - \sum_i N_i d \mu_i \quad [27] \]

Suitably substituting eqs. [17] and [18] in eq. [26] and eqs. [17] and [19] in eq. [27] at given \( T \) and \( P \), we obtain

\[ [d \mathcal{G}(T, P, \overline{N})]_{T, P} - \sum_{i=1}^4 N_i^d d \overline{N}_i \]

\[ = -kT \left( \sum_{i=1}^4 \frac{x_i^v}{x_i} d \ln a_i + d \ln a_M \right) \quad [28] \]

\[ 0 = \sum_{i=1}^4 x_i^v d \ln a_i + \sum_i x_i d \ln a_i \quad [29] \]

In general, the property of activity coefficient should be determined by what reference state to be chosen (see App. 3.3). It is reasonably possible to take the reference Gibbs free energy \( \overline{G} \) so as to satisfy the equation of the same form as the ideal eq. [7] for non-interacting micelles as follows,

\[ d \mathcal{G}(T, P, \overline{N}) = -dS_d T + dV_d P + \sum_{i=1}^4 \mu_i^v d \overline{N}_i \quad [30] \]

where non ideal \( \overline{S}, \overline{V} \) and \( \mu_i^v \) are defined at equilibrium as

\[ \overline{S} = -(\partial G / \partial T)_{T, \overline{N}} \]

\[ \mathbf{V} = (\partial G / \partial P)_{T, \overline{N}} \quad [31a, b] \]

\[ \mu_i^v(T, P, \overline{N}_i) = \left( \frac{\partial G_r}{\partial N_i} \right)_{T, P, \overline{N}_i} = \mu_i'(T, P, \alpha_i') \quad [31c] \]

Using eq. [30] in eq. [28] at given \( T \) and \( P \), we obtain

\[ 0 = \sum_{i=1}^4 x_i^v d \ln a_i^v + x_M d \ln a_M \quad [32] \]

From eqs. [29] and [32], we obtain the equations

\[ d \ln a_M = \sum r y_r d \ln a_r \quad [33] \]

\[ d \ln \gamma_M = \sum y_r d \ln \gamma_r \quad [34] \]

where has been used \( d \ln a_M = \sum y_r d \ln a_r \). From eq. [24a] and eq. [34], we obtain

\[ \sum y_r d \ln \eta_r = -\sum \ln \eta_r d y_r = 0 \quad [35] \]

from which we obtain the same form of equation as eq. [12]

\[ \sum \ln \gamma_r d y_r = 0 \quad [12^*] \]

It is apparent (App. 3.3) that eq. [35] should hold only if for all micellar species \( M \),

\[ \ln \eta_r = 0 \text{ i.e. } \gamma_r = \gamma_M \quad [36a, b] \]

It should be noted here, as will be shown later, that \( \gamma_r = \gamma_M \) for all \( M \), does not always mean the monodispersity of micelles such as suggested by Hall (5,7).

On the other hand, subtracting eq. [27] from eq. [26], we obtain another important equation

\[ d \mu_M = \sum y_r d \mu_r + \sum_{i=1}^4 \mu_i^v d \overline{N}_i \quad [37] \]

Substituting the exact differentials \( d \mu_r \) and \( d \mu_M \), obtained from eqs. [18] and [20] in eq. [37], and using eq. [24] in the result, we obtain essentially the same equation as eq. [10] derived by Hall.

\[ d \mathcal{G}(T, P, \overline{N}) = -S_d T + V_d P + \sum_{i=1}^4 \mu_i^v d \overline{N}_i - kT \sum \ln \eta_r d y_r \quad [38] \]

Taking the reference free energy \( \overline{G} \) so as to satisfy eq. [30] in eq. [38], we obtain eq. [35] and eq. [12*].

### 2.2 Size Distribution Function \( y_r \) of Micelles, \( \overline{N}_i \) and \( \beta \)

The number of counterions \( N_i^d \) bound to the rth micellar species \( M \), characterized by \((N_i^d, y_r)\) may be assumed to be a function of \( T \) and \( P \). Then the degree of
counterion binding $\beta_i (= N_i^c/N_i)$ of $M_i$ is to be a function of $T$ and $P$.

Putting $\ln \eta_i = 0$, we obtain from eqs. [21] and [22a]
\[ \mu_i^n = G_i + kT \ln \eta_i = \frac{3}{\iota_i} N_i^d \mu_i^n + \varepsilon_i M \] [39a, b]

The exact differential of $\mu_i^n$ is obtained from eqs. [39a] and [39b] as the followings
\[ d\mu_i^n = -S_i^n dT + V_i^n dP + kT d\ln \eta_i \] [40a]
\[ = \sum_{i=2}^{3} N_i^d d\mu_i^n + d\varepsilon_i + \mu_i^n dN_i^c \] [40b]

Multiplying eqs. [40a, b] we obtain the Gibbs-Duhem type equation for $M_i$ as the following.
\[ d\varepsilon_i = -S_i^n dT + V_i^n dP - \sum_{i=2}^{3} N_i^d d\mu_i^n + kT d\ln \eta_i \] [41]

where $\hat{S}_i^m$ and $\hat{V}_i^m$ are written as
\[ \hat{S}_i^m = S_i^m + \mu_i^n \left( \frac{\partial N_i^c}{\partial T} \right)_{p,y} \] [42a]
\[ = \sum_{i=2}^{3} N_i^d \hat{S}_i^m - \left( \frac{\partial \varepsilon_i}{\partial T} \right)_{p,y} \] [42b]
\[ \hat{V}_i^m = V_i^m - \mu_i^n \left( \frac{\partial N_i^c}{\partial P} \right)_{T,y} \] [43a]
\[ = \sum_{i=2}^{3} N_i^d \hat{V}_i^m + \left( \frac{\partial \varepsilon_i}{\partial P} \right)_{T,y} \] [43b]

where $\hat{S}_i^m = (\partial \mu_i^n / \partial T)_{p,y}$ and $\hat{V}_i^m = (\partial \mu_i^n / \partial P)_{T,y}$ are respectively the partial molecular entropy and volume of monomeric species $i$ in micelles. In these derivatives it has been used that constant $y_i$ is equivalent to constant $N_i (= \sum y_i N_i^c)$.

Multiplying eqs.[41], [42] and [43] by $y_i$ and summing over all $r$, we obtain
\[ d\varepsilon = -S dT + V dP - \sum_{r=2}^{3} N_r d\mu_r^n \] [44]
\[ \bar{S} = \sum_{r} y_r \bar{S}_r^m + \mu_r^n \sum_{r} y_r \left( \frac{\partial N_r^c}{\partial T} \right)_p \] [45a]
\[ = \sum_{r=2}^{3} N_r \bar{S}_r^m - \left( \frac{\partial \varepsilon_r}{\partial T} \right)_{p,y,sc} \] [45b]
\[ \bar{V} = \sum_{r} y_r \bar{V}_r^m + \mu_r^n \sum_{r} y_r \left( \frac{\partial N_r^c}{\partial P} \right)_T \] [46a]
\[ = \sum_{r=2}^{3} N_r \bar{V}_r^m + \left( \frac{\partial \varepsilon_r}{\partial P} \right)_{T,y,sc} \] [46b]

Subtracting eq. [44] from eqs.[41], we obtain on arrangement
\[ kT d\ln \beta_r = \left( \bar{S}^m - \bar{V}^m \right) dT - \left( \bar{V}^m - V \right) dP \]
\[ + \sum_{i=2}^{3} \left( N_i^d - N_i \right) d\mu_i \] [47]

where $d\mu_i^n = d\mu_i^n = d\mu_i$ has been used.

Substituting eqs. [42] and [45] in $\left( \bar{S}^m - \bar{V}^m \right)$ and eqs. [43] and [46] in $\left( \bar{V}^m - V \right)$, eq. [47] can be rewritten to another useful equation
\[ kT d\ln \eta_i = \sum_{i=2}^{3} \left( N_i^d - N_i \right) \left[ \bar{S}_i^m dT - \bar{V}_i^m dP + d\mu_i \right] \] [48]

Multiplying eq. [48] by $y_i N_i^c$ and summing over all $r$, we obtain the dependency of $\bar{N}_i$ on $T$, $P$ and $\mu_i$ in the following form.
\[ kT d\ln \bar{N}_r = \sum_{i=2}^{3} \left( \frac{N_i N_i^d}{N_r^d} - N_i \right) \left[ \bar{S}_i^m dT - \bar{V}_i^m dP + d\mu_i \right] \] [49]

where we have
\[ d\bar{N}_i = d\sum_{r} y_r N_r^c \quad N_r^{-} = \sum_{r} y_r N_r^c N_r^c \] [50a, b]

Multiplying eq. [48] by $y_i N_i^c$ and summing over all $r$, $kT d\ln \bar{N}_r =$
\[ \left[ \sum_{i=2}^{3} \left( \frac{N_i N_i^d}{N_r^d} - N_i \right) \bar{S}_i^m + \frac{1}{N_r^d} \left( \frac{\partial N_i}{\partial T} \right)_p \right] dT - \left[ \sum_{i=2}^{3} \left( \frac{N_i N_i^d}{N_r^d} - N_i \right) \bar{V}_i^m + \frac{1}{N_r^d} \left( \frac{\partial N_i}{\partial P} \right)_T \right] dP + \sum_{i=2}^{3} \left( \frac{N_i N_i^d}{N_r^d} - N_i \right) d\mu_i \]

where we have
\[ d\bar{N}_r = d\sum_{r} y_r N_r^c = \sum_{r} y_r N_r^c d\eta_r + d\bar{N}_r \] [52a]
\[ d\bar{N}_r = \sum_{r=2}^{3} \left( \frac{\partial N_r}{\partial T} \right)_p dT + \left( \frac{\partial N_r}{\partial P} \right)_T dP \] [52b]

Subtracting eq. [49] from eq. [51], we obtain an equation to express the dependency of the degree of counterion binding $\beta_i (= N_i^d/N_r^d)$ of ionic micelles as follows.
Multiplying eq. [41] by \( y_iN'_i \), summing over all \( r \) and suitably rearranging the result, we obtain the dependency of total concentration of monomeric 2 in micellar form on \( T, P \) and \( \mu \) as follows.

\[
d(N_2\alpha_m) = \frac{d\mu}{kT} \left[ \sum_{r=2} N_rN'_r N''_r \right] + \sum_{r=2} \frac{N_rN'_r N''_r - N_rN''_r - N'_rN''_r}{kT} \left( \frac{\partial \ln \alpha_m}{\partial T} \right)_{P, \mu} \, dT + \frac{d\mu}{kT} \sum_{r=2} \frac{N_rN'_r d\mu_i}{N_2} \, [54]
\]

It will be found that eq. [54] is the equation useful to treat the temperature and pressure effects on solubility of ionic surfactants in water (17), which will be reported elsewhere.

It should be noted here that eqs. [39] ~ [54] have been derived for polydispersed micelles on the basis of the condition \( \gamma_i = \gamma_m \). It is obvious here that \( \gamma_i = \gamma_m \) does not always mean the monodispersity of micelles as suggested by Hall (5,7).

### 2.3 The Degree of Counterion Binding \( \beta \) of Ionic Micelles

Using \( d\epsilon = 0 \) and \( d\mu_i'' = d\mu_i' \) at complete equilibrium and \( d\mu_i' = kT d\ln a_i^0 \) in eq. [44] at given \( T \) and \( P \), and rearranging the result, we obtain

\[
d\ln a_i^0 = -\beta d\ln a_i^0 + \frac{1}{N_2} d\ln \alpha_m \quad [55]
\]

When an added electrolyte \( X_{34} \) is present, we have two independent variables among \( d\ln a_i^0 \), \( d\ln a_i^2 \) and \( d\ln \alpha_m \) at given \( T \) and \( P \) (App. 3·1). In order to compare physicochemical property among solutions, it is reasonable to take a series of micellar solutions with the same value of \( \alpha_m \) at different concentrations of added electrolyte \( X_{34} \) at given \( T \) and \( P \). Putting \( d\ln \alpha_m = 0 \) in eq. [55], we obtain the equation to express the dependency of \( \ln a_i^0 \) on \( \ln a_i^2 \) in such a series of ionic micellar solutions at given \( T \) and \( P \) and \( \alpha_m \).

\[
d\ln a_i^2 = -\beta d\ln a_i^0 \quad [56]
\]

If \( \beta = \beta(T, P, \alpha_m) \), eq. [56] can be integrated at given \( T \) and \( P \) and \( \alpha_m \) to a linear equation with an integral constant \( I(T, P, \alpha_m) \) as follows.

\[
\ln a_i^2 = -\beta \ln a_i^0 + I(T, P, \alpha_m) \quad [57]
\]

Linearity of eq. [57] at given \( T \) and \( P \) and \( \alpha_m \) has experimentally been verified (12).

If the ionic micelles have sufficiently large \( N_2 \) so that \( N_2^{-1} d\ln \alpha_m \) may relatively be ignored in eq. [55], eq. [56] and the equation of same form as eq. [57] also hold to good approximation at given \( T \) and \( P \).

As mentioned in the introduction, approximately linear decrease of \( \ln a_i^0 \) with increase of \( \ln a_i^2 \) at given \( T, P \) is the experimental fact that has been found in various ionic surfactants (8-11). It can be concluded from these that \( \beta = \beta(T, P, \alpha_m) \), or \( \beta = \beta(T, P) \) for micelles with sufficiently large \( N_2 \).

Condition for \( \beta \) to be constant is discussed here in the following way. At given \( T \) and \( P \), eq. [53] can be rewritten as follows.

\[
d\ln \beta = \sum_{i=2}^3 \left( \frac{N_iN_i}{N_3} - \frac{N_iN_i'}{N_2} \right) d\ln a_i^0 \quad [58a]
\]

\[
e^{\sum_{i=2}^3 \ln N_i} \left[ \frac{N'_i}{N_3} - \frac{N'_i}{N_2} \right] d\ln a_i^0 \quad [58b]
\]

where is used \( d\mu_i = d\mu_i' = kT d\ln a_i^0 \) at given \( T \) and \( P \). Estimating \( d\ln a_i^0 \) from eq. [58] by the use of eq. [55], we obtain

\[
d\ln \beta = \left( \frac{N_2N_i}{N_3} - \frac{N_2N_i'}{N_2} \right) \frac{1}{N_2} d\ln \alpha_m
\]

\[
+ N_2 \left( \frac{N_iN_i}{N_3} - \frac{2N_iN_i'}{N_2} + \frac{N_iN_i'}{N_2} \right) d\ln a_i^0
\]

\[
= \sum_{i=2}^3 \ln N_i \left( \frac{N'_i}{N_3} - \frac{N'_i}{N_2} \right) \frac{1}{N_2} d\ln \alpha_m
\]

\[
+ \sum_{i=2}^3 \left( \frac{N'_i}{N_3} - \frac{N'_i}{N_2} \right)^2 \frac{N_i}{N_2} d\ln a_i^0
\]

In order that \( \beta \) may be constant for a series of micellar solutions at given \( T, P \) and \( \alpha_m \), or for solutions of ionic micelles with large \( N_2 \) enough for \( N_2^{-1} d\ln \alpha_m \) to approximately be ignored in eq. [55], it is necessary to have

\[
\left( \frac{\partial \ln \beta}{\partial \ln a_i^0} \right)_{T, P} = \left( \frac{\partial \ln \beta}{\partial \ln a_i^0} \right)_{T, P, \alpha_m}
\]

\[
= N_2 \sum_{i=2}^3 \left( \frac{N'_i}{N_3} - \frac{N'_i}{N_2} \right)^2 = 0
\]

It is mathematically evident that eq.[60] holds only if for all \( r \)
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\[
\left( \frac{N'_i}{N_3} - \frac{N'_j}{N_2} \right)^2 = 0 \text{ i.e. } \frac{N'_i}{N_3} - \frac{N'_j}{N_2} = 0
\]

Eq. [61b] holds only if

\[
\beta_r = \frac{N'_i}{N'_j} \frac{N'_j}{N_2} = \beta \text{ (for all } r) \quad \text{[62]}
\]

where \(\beta\) is the degree of counterion binding of the \(r\)th micellar species \(M_r\).

It is seen from eq. [59b] that if eq. [62] holds for our polydispersed micelles, \(\beta\) does not depend on \(a_M\) and \(a_i^0\) at given \(T\) and \(P\) i.e. \(\beta = \beta(T, P)\). And the linear decrease of \(\ln a_i^0\) with increase of \(\ln a_i^0\) at given \(T\) and \(P\) (8-11) can well be explained from ionic micelles having such size distribution as characterized by eq. [62] that shows \(\beta\), being independent of micelle size \(N_r^0\). This seems to be intimately related as characterized by eq. [62] that shows \(\beta\), being independent of micelle size \(N_r^0\). Needless to say, constant \(\beta = \beta(T, P)\) just holds for monodispersed micelles.

On the other hand, eliminating \(d\ln a_i^0\) from eq. [58a] by use of eq. [54] at given \(T\) and \(P\), we obtain an equation equivalent to eq. (80) in ref. (15) of Hall.

\[
d\alpha = \left( \frac{N_1}{N_2} - \frac{N'_1}{N'_2} \right) d\ln (N_2 a_M) + \left( \frac{N'_1}{N_2} - \frac{N'_1}{N'_2} \right) d\ln a_i^0
\]

where \(\alpha = 1 - \beta\). The condition for \(\alpha\) to be kept constant with the change of counterion concentration is mathematically given as follows.

\[
\left( \frac{\partial \alpha}{\partial \ln a_i^0} \right)_{T, P, N, a_M} = \frac{1}{N_2 N_3^2} (N_2 N_3 - N'_2 N'_3) = 0 \quad \text{[64]}
\]

from which we obtain just the same condition as eq. [62] (App. 3.4).

It is problematic that Hall (15) daringly avoided to directly examine the mathematical condition [64] for \(\alpha\) to be constant, and made roundabout and ambiguous discussion in order to explain that \(\partial \alpha / \partial \ln a_i^0 = 0\).

The following relations hold under the condition [62] at given \(T\) and \(P\).

\[
N_2 N_3 = \sum y_i N'_i N'_j = \sum y_i \beta (N'_i)^2
\]

\[
\frac{N_2}{N_3} = \beta \frac{N'_i}{N'_j}
\]

At given \(T\) and \(P\), eqs. [48] and [49] are rewritten to

\[
d\ln y_i = (N'_i - N'_j) d\ln a_i^0 (a_i^0) = 0
\]

\[
= \frac{N'_i - N'_j}{N'_j} d\ln a_i^0
\]

\[
d\ln N_2 = \frac{N'_2 - N'_j}{N'_j} d\ln a_i^0
\]

Eq. [67] shows that \(N_2\) increases with increase of \(a_M\) owing to the promotion of micelle formation at given \(T\) and \(P\), on which \(\beta\) is kept constant under the condition [62]. The increase of \(N_2\) with the promotion of micelle formation by the addition of electrolyte is experimentally verified (18, 19).

Eqs. [66] and [67] have been derived for polydispersed micelles consistently based on eqs. [12] resulting in eq. [36b]; \(\gamma_r = \gamma_M\). It is evident from this that the ionic micelles for which \(\gamma_r = \gamma_M\) holds are usually polydispersed micelles characterized by \(\beta = \beta\) for all micellar species \(M_r\), in stead of being monodispersed micelles as suggested by Hall (5, 7).

2.4 To Treat \(a_i^0\), \(a_i^0\) and \(a_M\) as the Functions of the Total Concentrations \(C_2^i\) and \(C^i\)

It is useful to express the activities as the functions of total concentrations \(C_i\) and \(C^i\). Here we define the following concentrations denoted by \(c\) or \(C\).

\[
c_i = \frac{N'_i}{N'_1} \quad c_M = \frac{N_M}{N'_1} \quad C_i = \frac{N'_i}{N'_1}
\]

where \(c_i = x_i^0\) and \(c_M = x_M\) are good approximations in solutions not so concentrated in micelles. We have the following equations of mass balance in micellar solutions.

\[
\begin{align*}
C_i' &= c_i + c_M N_r \quad i = 2, 3 \\
C_i' &= C_2 + C_X
\end{align*}
\]

where \(C_X\) is the concentration of added electrolyte \(X_{iX}\). When \(C_X \gg C_2^i\), as is usual in experiments, we have \(C_i' = C_X = c_i\). Procedures from now on are along lines similar to Hall’s method applied to treat ideal multi-component micelles of nonionic surfactant (6).

At given \(T\) and \(P\), eq. [54] is rewritten for \(k\) as follows

\[
d(a_M N_k) = \sum a_M N_i N_k d\ln a_i^0
\]

which can be rewritten
Using eq. [71b], we obtain from eq. [69]
\[ dC_i' = C_i'd\ln C_i' = dc_i + d(\bar{N}_s c_m) \]
\[ = c_i'd\ln a_i' + \sum_{j=1}^{3} c_{ij} N_s N_j d\ln a_i' - C_i'd\ln \gamma_i' \]  [72b]
Eq. [72b] is rewritten to
\[ C_i'd\ln a_i' = c_i'd\ln a_i' + \sum_{j=1}^{3} c_{ij} N_s N_j d\ln a_i' \]
where we have
\[ A_i' = C_i'\gamma_i' \]  [74a]
\[ C_i'd\ln \gamma_i' = c_i'd\ln \gamma_i' + c_m\bar{N}d\ln \gamma_m \]  [74b]

In solutions dilute in micelles, to omit the last term in eq. [72b] will not bring about so large error in the discussions hereafter. It will not be so rough approximation to write \( dC_i' \) for \( k = 2,3 \) at given \( T \) and \( P \) as follows.
\[ dC_i' = (c_i + c_m \bar{N}_i') d\ln a_i' + c_m N_s N_j d\ln a_i' \]  [75]
\[ dC_i' = c_m N_s N_j d\ln a_i' + (c_i + c_m \bar{N}_i') d\ln a_i' \]  [76]
Solving eqs. [75] and [76] simultaneously for \( d\ln a_i' \) and \( d\ln a_i' \) in terms of \( dC_i' \) and \( dC_i' \), we obtain in good approximation
\[ d\ln a_i' = D^{-1} \left[ (c_i + c_m \bar{N}_i') dC_i' - c_m N_s N_j dC_i' \right] \]  [77]
\[ d\ln a_i' = D^{-1} \left[ (c_i + c_m \bar{N}_i') dC_i' - c_m N_s N_j dC_i' \right] \]  [78]
where \( D \) is the determinant made of the coefficients of \( d\ln a_i' \) and \( d\ln a_i' \) at the right hand side of the simultaneous equations [77] and [78],
\[ D = (c_i + c_m \bar{N}_i')(c_i + c_m \bar{N}_i') - c_m N_s N_j N_k \]  [79]
Substituting eqs. [77] and [78] in [55], we obtain
\[ d\ln a_m = D^{-1} \left[ \bar{N}_i(c_i + c_m \bar{N}_i') - c_m N_s N_j N_k \right] dC_i' + \]
\[ D^{-1} \left[ \bar{N}_j(c_i + c_m \bar{N}_i') - c_m N_s N_j N_k \right] dC_j' \]  [80]

It should be noted here that we are treating polydispersed ionic micelles with constant \( \beta \) under the condition [62]. Using eq. [65] and \( dC_i' = dC_i' + dC_X \), eq. [80] is simplified to
\[ d\ln a_m = \bar{N}_s d\ln a_i'(a_i')^\beta \]  [81a]
\[ = D^{-1}(c_i + c_m \bar{N}_i') dC_i' + D^{-1}c_i \bar{N}_s dC_X \]  [81b]

Using \( c_2 \ll c_3 = C_X \) for sufficiently large concentration of added electrolyte as is usually the case, \( D \) is to good approximation simplified to
\[ D = c_1(c_2 + c_m \bar{N}_i') \]  [82]
From eqs.[67] and [81b], we obtain at given \( T \) and \( P \)
\[ d\bar{N}_2 = \left( \bar{N}_i^2 - \bar{N}_i^2 \right) d\ln a_i'(a_i')^\beta = \frac{\bar{N}_i^2 - \bar{N}_i^2}{\bar{N}_2} d\ln a_m \]
\[ = \left( \bar{N}_i^2 - \bar{N}_i^2 \right) D^{-1} \left[ (c_2 \beta + c_3) dC_i' + c_2 \beta dC_X \right] \]  [83]
Eq. [83] shows that \( \bar{N}_2 \) increases with increase of \( C_X \) at given \( C_i' \), and increases with increase of \( C_i' \) at given \( C_X \). The increase of \( \bar{N}_2 \) with \( C_X \) is consistent with the behavior of weight average aggregation number as is obtained from the intercept of assumed linear Debye plot in the light scattering of micellar solutions of various ionic surfactants (18,19). While the increase of \( \bar{N}_2 \) with increase of \( C_i' \) at given \( C_X \) is not consistent with the assumed linearity of Debye plots which requires the aggregation number to be kept constant.

It has been found that Debye plots for micellar solutions of various nonionic surfactants are not linear, especially in the vicinity of \( CMC \), which is well explained by the increase of \( \bar{N}_2 \) with increase of \( C_i' \) (20). It seems necessary to strictly reexamine the applicability of assumed linear Debye plot to get the mean aggregation number of completely open \( (T, P, \mu) \) systems in solution.

Eq. [67] shows that \( \bar{N}_2 \) of monodispersed micelles is kept constant with promotion of micelle formation. It is apparent that only if micelles are monodispersed, mass action law holds for the formation of ionic micelles in the form \( \bar{N}_2D_2 + \bar{N}_2D_2 = M \). It seems problematic that Philips (19) assumed the monodispersity of ionic micelles and used the law of mass action in his excellent definition of \( CMC \).

2.5 Critical Micellization Range (CMR) and Critical Micelle Concentration (CMC)

In experiments to measure \( CMC \), \( C_i' \) is usually made increase at given \( C_X \). Using approximately eq. [82] for \( D \), we obtain the following equation from eq. [81].
\[ \frac{\partial \ln a_i'(a_i')^\beta}{\partial \ln C_i'} = \frac{c_2 + c_m \bar{N}_i'}{c_2 + c_m \bar{N}_i'} \]  [84]
where is assumed that \( c_3 \) is much larger than \( c_2 \) as is
usual in experiments.

Using eq. [65], we obtain the following equation from eq. [54] at given \( T \) and \( P \)

\[
d(N_2) = a_m N_2^2 d \ln a'_2(a'_1)^b
\]  

[85a]

From eq. [84] and eq. [85a] we obtain

\[
\frac{\partial (a_m N_2^2)}{\partial C'_1} = \frac{a_m N_2^2}{c_2 + c_m N_2^2}
\]  

[85b]

Eq. [84] shows that if \( N_2 \) and \( N_2^2 \) are large, once \( a_m \) has reached only a small value with increasing \( C'_1 \), \( \frac{[\partial \ln a'_2(a'_1)^b]}{\partial \ln C'_1} \) will fall from \( = 1 \) to a small value \( = \frac{N_2}{N_2^2} \) over a narrow range of \( C'_1 \). Such a narrow range of \( C'_1 \) is referred to as critical micellization range (CMR). Eq. [85b] shows that \( \frac{\partial (a_m N_2^2)}{\partial C'_1} \) increases rapidly from 0 to 1 with increase of \( C'_1 \) in the (CMR) as mentioned above.

It is convenient to define CMC as the total concentration \( C'_1 \) of surface active ion 2 at a point within (CMR) at given \( T, P \) and \( C_v \). Such a definition of (CMR) is quite arbitrary, but should correspond to a concentration easily identified by experiment.

Definitions of CMC have been given by Phillips (19) and Corrin (21). Along lines similar to the definition of Phillips, CMC may be taken to as being a point satisfying the following condition in (CMR).

\[
\frac{\partial \ln a'_2(a'_1)^b}{\partial \ln C'_1} = \frac{c_2 + c_m N_2}{c_2 + c_m N_2^2} = 0.5
\]  

[86]

from which we obtain the relations at CMC

\[
c_m = c_2 / (N_2^2 - 2N_2) = c_2 / N_2^2
\]  

[87]

Putting the right hand side of (85b)=0.5, we also obtain the same relation as eq. [87].

### 2.6 Corrin-Harkins Equation

It is possible to take points having a certain same value of \( a_m \) in the respective (CMR)s for different concentrations of added electrolyte at given \( T \) and \( P \). It is evident that eq. [56] should also hold for such a series of solutions of the same \( a_m \) in respective (CMR)s. If our polydisperse ionic micelles have constant \( \beta \) under the condition [62] within the CMRs, eq. [56] can be integrated at given \( T, P \) to a linear equation of the same form as eq. [57]. CMC is defined as the total surfactant concentration \( C_3 \) at a point \( (a_2, a_3) \) of a certain same value of \( a_m \) within the (CMR) for a given concentrations \( C_x \) of added electrolyte.

Corrin-Harkins equation can to rough approximation be derived from eq. [57] in the following way. Since CMC is usually very small and as shown in eq. [87], \( c_m \ll c_2 < c_3 \) at \( C'_2 = \text{CMC} \), the following rough approximations may be made.

\[
a'_2 = \text{CMC} \quad a'_1 = (\text{CMC}) + C_x
\]  

[88a, b]

Substituting eq.[88a, b] in eq.[57], we can presume an equation of Corrin-Harkins type.

\[
\ln(\text{CMC}) = -\beta_{CH} \ln((\text{CMC}) + C_x) + I_{CH}
\]  

[89]

If linearity holds for eq. [89], it is most probable that \( \beta_{CH} \) will approximately be equal to \( \beta = \frac{N_3}{N_2} \).

Strictly, Corrin-Harkins equation should be derived by the variable transformation from \( (a_2', a_3') \) to \( (C'_2, C'_3) \) in eq. [56] by the use of eqs. [77] and [78], and the transformation of \( (C'_2, C'_3) \) to \( ([\text{CMC}], (\text{CMC})+C_x) \) by the use of the definition of CMC. Eq. [80] is the equation useful for this procedure.

It should be noted that problematic phase separation model (22) for micelle formation is never used here to treat the Corrin-Harkins equation.

#### 2.6.1 Corrin-Harkins equation and the definition of CMC

Firstly, putting \( d \ln a_m = 0 \) in eq. [80], we obtain the following equation to show the dependency of \( \ln C'_1 \) on \( \ln C'_3 \) in a series of micellar solutions with a certain same value of \( a_m \) at given \( T \) and \( P \).

\[
d \ln C'_3 = -\hat{\beta} d \ln C'_1
\]  

[90]

where we have

\[
\hat{\beta} = \left( \frac{\partial \ln C'_3}{\partial \ln C'_1} \right)_{T, P, a_m}
\]

\[
= \frac{C'_1 \left( c_2 + c_m N_2^2 \right) - c_m N_2 N_3}{C'_1 \left( c_3 + c_m N_3^2 \right) - c_m \beta N_2 N_3}
\]  

[91a, b]

If our polydisperse ionic micelles have constant \( \beta \) under the condition [62] from which eqs.[65a, c] are derived, eq. [91] can be simplified to

\[
\hat{\beta} = \frac{c_2 C_3}{c_3 C_2} \beta = \frac{c_2 (c_1 + c_m N_1)}{c_3 (c_2 + c_m N_2)} \beta
\]  

[92]

It is apparent from eqs. [91] and [92] that \( \hat{\beta} \) is not generally constant at \( T, P \) and \( a_m \). Then eq. [90] shows that \( \ln C'_3 \) does not linearly decrease with increase of \( \ln C'_1 \) at given \( T, P \) and \( a_m \).
It is possible here to take a series of micellar solutions at CMCs for different added electrolyte concentrations, (CMCs) being respectively defined as the total surfactant concentrations at points of a certain same value of $a_M$ within the respective(CMR)s. It is apparent that eq. [90] and eq. [92] should also hold for such a series of micellar solutions at CMCs. Since $c_M$ is so small compared with $c_2$ at CMC within (CMR) as shown in eq. [87] that $C_2^* = c_2$ and $C_3^* = c_3$ may hold, it is just a good approximation that $C_2^* / C_3^* = 1$ at CMC

Then we have in eq. [92]

$$\beta = \beta \text{ at CMC} \tag{93}$$

We just have at CMC

$$C_2 = (\text{CMC}) \quad C_3 = (\text{CMC}) + C_x \quad \text{[95a, b]}$$

Using eqs. [94] and [95a, b] in eq. [90], we obtain

$$d \ln (\text{CMC}) = -\beta d \ln [(\text{CMC}) + C_x] \quad \text{[96]}$$

Eq. [96] can be integrated in good approximation to the following equation at given $T$, $P$ and $a_M$

$$\ln (\text{CMC}) = -\beta \ln [(\text{CMC}) + C_x] + \hat{I}(T, P, a_M) \quad \text{[97]}$$

It can be seen from eq. [97] that the plot of $\ln (\text{CMC})$ against $\ln [(\text{CMC}) + C_x]$ at given $T$, $P$ and $a_M$ is to very good approximation linear, and that the gradient obtained is approximately equal to constant $\beta$.

If $N_2$ is sufficiently large that $N_2^\dagger d \ln a_M$ may be ignored in eq. [55] and eq. [80], the following equation of the same form as eq. [97] can approximately be derived in the same procedure as above.

$$d \ln (\text{CMC}) = -\beta d \ln [(\text{CMC}) + C_x] + \hat{I}(T, P) \quad \text{[98]}$$

in which CMC may be determined as a point suitably taken in (CMR) at given $T$, $P$ and $C_x$. Eq. [98] is just the Corrin-Harks equation. It should be noted here that the available experimental data of CMC may have sufficient arbitrariness to make eq. [98] be linear at given $T$ and $P$.

2.6.2 Another definition of CMC and Corrin-Harks equation

At given $T$ and $P$, eq. [54] and eq. [75] can to good approximation be rewritten to

$$d \ln (c_M N_2) = \frac{N_2^*}{N_2} d \ln a_M^* + \frac{N_3 N_2}{N_2} d \ln a_M^* \quad \text{[99]}$$

$$d \ln C_2^* = \frac{c_2 + c_M N_2^*}{C_2^*} d \ln a_M^* + \frac{c_M N_3 N_2}{C_2^*} d \ln a_M^* \quad \text{[100]}$$

Subtracting eq. [100] from eq. [99], we obtain

$$d \ln \xi = \frac{c_2(\frac{N_2^*}{N_2} - N_2)}{C_2^* N_2} d \ln a_M^* + \frac{c_2 N_3 N_2}{C_2^* N_2} d \ln a_M^* \quad \text{[101]}$$

$$\xi = \left( \frac{c_M N_2}{C_2^*} \right) \quad \text{[102]}$$

where $\xi$ may be defined as the degree of micellization at given $T$ and $P$.

Putting $d \ln \xi = 0$ in (101), we obtain the following equation that holds for a series of micellar solutions at the same degree of micellization $\xi$ at different concentrations of added electrolyte.

$$d \ln a_M^* = -\frac{N_3 N_2}{N_2^* - N_2} d \ln a_M^* \quad \text{[103a]}$$

$$= -\frac{N_3 N_2}{N_2^*} d \ln a_M^* \quad \text{[103b]}$$

If our polydisperse ionic micelles are approximately under the condition [62] to result in eqs. [65a, c] at given $T$ and $P$, we have

$$\frac{N_2 N_3}{N_2^*} = \frac{N_3}{N_2} = \beta(T, P) \quad \text{[104]}$$

Then we are to obtain the equations of the same form as eq. [56] and eq. [57] from eqs. [103] and [104] at given $T$, $P$ and $\xi$ as follows,

$$d \ln a_M^* = -\beta d \ln a_M^* \quad \text{[105]}$$

$$\ln a_M^* = -\beta \ln a_M^* + I(T, P, \xi) \quad \text{[106]}$$

which show that condition $(T, P, \xi)$ is approximately equal to the condition $(T, P, a_M^*)$ when $\beta$ is kept constant under the condition [62] at given $T$ and $P$.

Substituting eq. [77] and eq. [78] for $d \ln a_M^*$ and $d \ln a_M^*$ in eq. [105], we obtain

$$d \ln C_2^* = -\beta * d \ln C_2^* \quad \text{[107]}$$

where $\beta^*$ is defined as

$$\beta^* = \left( \frac{\partial \ln C_2^*}{\partial \ln C_3} \right)_{T, P, \xi}$$

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\[ \frac{C_t}{C_2} = \frac{Bc_2 + c_m \left( \beta N t^2 - N e N i \right)}{c_2 + c_m \left( N t^2 - \beta N t^2 N e \right)} \]  

which can approximately be simplified to by the use of eq. [65]

\[ \beta^* = \left( \frac{c_2 C t}{c_2 C 2} \right) \beta \]  

It is seen from eqs. [107] and [108b] that since \( \beta^* \) is not generally constant, \( \ln C_t \) does not linearly decrease with increase of \( \ln C_2 \) at given \( T, P \) and \( \xi \).

Another critical micelle concentration (CMC)* can be taken to the total concentration \( C_2 \) at a point having a certain suitable value of \( \xi \) in the (CMR) at given \( T, P \) and \( C_X \). Equations of the same forms as eqs. [106], [107] and [108] should also hold for a series of micellar solutions at (CMC)*s for different added electrolyte concentrations at given \( T \) and \( P \). Since eq. [93] may also holds at (CMC)*s, we are to have at (CMC)* in eq. [108b]

\[ \beta^* = \beta \]  

Then for a series of micellar solutions at various (CMC)*s, we have

\[ d \ln (CMC)^* = -\beta d \ln[(CMC)^* + C_X] \]  

Eq. [110] can be integrated to an approximately linear equation of Corrin-Harkins type with respect to (CMC)*s as the following.

\[ \ln(CMC)^* = -\beta \ln[(CMC)^* + C_X] + I^* (T, P, \xi) \]  

2.6.3 Linearity of Corrin-Harkins plot and \( \beta \)

According to the two kinds of definition of critical micelle concentration, linear equations [98] and [111] of Corrin-Harkins type have theoretically been derived from eq. [56], in which the polydispersed ionic micelles are assumed to have constant degree of counter ion binding \( \beta \) under the condition [62] at given \( T \) and \( P \). \( \beta = \beta(T, P) \) has been concluded from eq. [56] and the experimental results (8-12) that show linear decrease of \( \ln(\alpha)^* \) with increase of \( \ln(\alpha)^* \).

It can then be concluded here that if a linear Corrin-Harkins plot is obtained by the use of CMC data precisely measured, the gradient \( \beta \) obtained can to good approximation presume the mean degree of counterion binding of micelles in solutions not only at CMC but also at surfactant concentrations higher than CMC. And the ionic micelles in solution which give linear Corrin-Harkins plot may be regarded to have polydispersity characterized by the condition [62], which is consistent with \( \gamma_r = \gamma_m \) for all \( M_r \). Conditions [12] or [33] resulting in \( \gamma_r = \gamma_m \) do not always mean the monodispersity of micelles as has been suggested by Hall (5,7).

It should be noted here that according to the width of critical micelleization range, experimental CMC data may have sufficient arbitrariness so as to make Corrin-Harkins plot be linear, and they will not have so high accuracy as to distinguish between eqs. [98] and [111].

Complete set of thermodynamic parameters for micellar solutions, \( a'_m, a_m N_i \) and \( N, N_i \) can in principle be obtained from analyzing the light scattering data of micellar solutions by a suitable equation of light scattering (24) and the small system thermodynamics (6) (20,23).

Ooi’s light scattering equation (25) is useful to analyze the light scattering data of micellar solutions of an ionic surfactant with an electrolyte added at sufficiently high concentration (6,12), in which the free counterion concentration can to good approximation be treated as equal to the concentration of added electrolyte.

3 Appendix

3.1 Introduction to Small System Thermodynamics of Micelles in Solution

Small system thermodynamics (1-3) gives the following equation to an ensemble of \( N_m \) polydispersed c component micellar small systems in solution.

\[ dG_i = -S_i dT + V_i dP + \sum_{i=1}^{\infty} \mu_i dN_i^c + \sum_{i=1}^{\infty} \mu_i^r dN_i^e + \epsilon dN_M \]  

\[ \epsilon = \left( \frac{\partial G_M}{\partial N_M} \right)_{T,P,N,N^c} \]  

\( \epsilon \) is referred to the subdivision potential of micellar small systems.

[A1] is rewritten to

\[ dG_i = -S_i dT + V_i dP + \mu_i dN_i^c + \sum_{i=2}^{\infty} \mu_i^r dN_i^e + \epsilon dN_M \]  

\[ \mu_M = \left( \frac{\partial G_M}{\partial N_M} \right)_{T,P,N,N^c} = \sum_{i=1}^{\infty} \mu_i^r N_i^c + \epsilon \]  

When our micelles have polydispersity characterized by the numbers \( N_i \) of rth micellar species \( M_r \), containing

$N'_i$ of the monomeric component $i$, the following relations hold.

$$N''_i = N_M N_i = \sum N_i N'_i \quad \mathbf{\mathbf{N}}_i = \sum y_i N'_i \quad \text{[A5a, b]}$$

where $y_i$ is the probability distribution function of poly-dispersed micelles defined as

$$y_i = N_i / \mathbf{N} \quad \text{[A5c]}$$

Using [A5], [A1] is rewritten to

$$dG_i = -S_i dT + V_i dP + \sum \mu'_i dN'_i + \sum \mu_i dN_r$$

$$\mu_r = \left( \frac{dG_r}{dN_r} \right)_{T, r, N_r} = \sum \mu''_i N'_i + \varepsilon \quad \text{[A6]}$$

It should be noted here that $T, P, N'_i(= N'_i + N''_i = N'_i + \sum N'_i N'')$ are experimentally determinable variables. Condition that $G_i$ is a minimum at given values of these experimental variables is derived from [A1], [A3] and [A6] as follows.

$$[dG_i]_{T, P, N_r} = \sum (\mu'_i - \mu''_i) dN'_i + \varepsilon dN_M$$

$$= \left( \mu_M - \sum \mu'_i \mathbf{N}_i \right) dN_M + \sum \mu''_i dN_r$$

$$= \sum (\mu_r - \sum \mu'_i N'_i) dN_r = 0$$

which hold respectively if

$$\mu'_i - \mu''_i = \mu_r - \sum \mu'_i N'_i = 0 \quad \text{[A8a, b]}$$

$$\mu_M = \sum \mu'_i \mathbf{N}_i, \quad \mu_r = \sum N'_i \mu'_i \quad \text{[A9a, b]}$$

The equilibrium here is referred to as complete equilibrium (3).

Since an ensemble of $N_M$ icelles in solution is macroscopic in nature, $G_i$ should be a linear homogeneous function of $N'_i, N''_i$ and $N_M$ in [A1], or of $N'_i$ and $N_M$ in [A3] or of $N''_i$ and $N_r$ in [A6]. Then we obtain

$$G_i = \mu_i N'_i + \sum \mu'_i N'_i + \sum \mu''_i N''_i + \varepsilon N \quad \text{[A10]}$$

$$G_i = \mu_i N'_i + \sum \mu'_i N'_i + \mu_M N \quad \text{[A11]}$$

$$G_r = \sum \mu'_i N'_i + \sum \mu_r N_r \quad \text{[A12]}$$

From [A1] and the exact differential of [A10] we obtain a Gibbs-Duhem type equation

$$d\varepsilon = -S_r dT + V_r dP - \sum N'_i d\mu'_i - \sum N''_i d\mu''_i \quad \text{[A13]}$$

From [A3] and the exact differential of [A11] and from [A6] and the exact differential of [A12], we obtain the other types of Gibbs-Duhem equation, eq. [1a] and eq. [2a].

We try to apply these equations to micellar solution of single component ionic surfactant $D_{23}$ with an electrolyte $X_{24}$ added. Using the conditions [A8a, b] for complete equilibrium of the formation of ionic micelles, [A13] can be rewritten as

$$0 = -S_r dT + V_r dP - \sum N'_i d\mu'_i - N'_2 d\mu''_2 - N'_3 d\mu''_3 \quad \text{[A14]}$$

where $N'_2 = N''_2 + N_2$ and $N'_3 = N'_2 + N_M$ and $\mu_2(= \mu_3 + \mu_4)$ and $\mu_3(= \mu_3 + \mu_4)$ are respectively the chemical potentials of ionic surfactant $D_{23}$ and that of added electrolyte.

[A14] shows that an aqueous micellar solution of single component ionic surfactant $D_{23}$ with an electrolyte $X_{24}$ added should have 2 independent variables at complete equilibrium at given $T$ and $P$.

### 3.2 About Eq. [18] and Eq. [30]

It is reasonable to assume for $a'_i = x'_i \gamma'_i$ and $a_M = x_M \gamma_M$ to satisfy eq. [32], which has the same mathematical form as the identical equation

$$0 = \sum x'_i d \ln x'_i + x_M d \ln x_M$$

Substituting eq. [17] for $\mu'_i$ in eq. [26] at given $T$ and $P$, and using eq. [32] in the result, we obtain

$$[d(\mu_M - kT \ln a_M)]_{T, P} = \sum \mu'_i d \mathbf{N}_i \quad \text{[A15]}$$

[A15] shows that $(\mu_M - kT \ln a_M)$ is a function of $T, P$ and $\mathbf{N}_i$. Let it be $G(T, P, \mathbf{N}_i)$. We at once obtain the same form of equation as eq. [18] for $\mu_M$

$$\mu_M = G(T, P, \mathbf{N}_i) + kT \ln a_M \quad \text{[A16]}$$

and [A15] is rewritten to

$$[dG(T, P, \mathbf{N}_i)]_{T, P} = \sum \mu'_i d \mathbf{N}_i \quad \text{[A17]}$$

from which we can resultantly derive the same form of equation as ideal eq. [7].

### 3.3 About $\gamma_r = \gamma_M$ for All $r$

Using $dy_r = -\sum dy_r (r \neq p)$ for an arbitrary $p$, eq. [35] is rewritten to

$$\sum_{r \neq p} (\ln \eta_r - \ln \eta_p) dy_r = 0 \quad \text{[A18]}$$

Since $dy_r (r \neq p)$ are all independent, [A18] holds only if for all $r (\neq p)$
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\[ \ln \eta_r = \ln \eta_p \text{ i.e. } \ln \gamma_r = \ln \gamma_p \quad [A19] \]

From [A19] and the definition of \( \gamma_M \) in eq. [24b], we obtain \( \gamma_r = \gamma_M \) for all \( r \).

### 3.4 About Hall’s Equation (80) in the Ref. 15

Using the present notations and the definition of \( \beta \), Hall’s equation (80) for \( \alpha = 1 - \beta \) in ref. 15 may be written as the following.

\[
\begin{align*}
d\alpha &= \left( \frac{N_3}{N_2} - \frac{N_2^2 N_3}{N_3^2} \right) d\ln(N_2 a_M) \\
+ &\frac{1}{N_2 N_3^2} \left( \frac{N_2^2 N_3^2 - N_2 N_3^2}{N_2 N_3^2} \right) d\ln a_i^r
\end{align*}
\]

\[ [A20] \]

In order that we may have in [A20]

\[
\left( \frac{\partial \alpha}{\partial \ln a_i^r} \right)_{r, \beta, \gamma, \mu} = 0 \quad [A21]
\]

it is necessary to have

\[
0 = \frac{N_2^2 N_3^2 - N_2^2 N_3^2}{N_2 N_3^2} = \sum_r y_r (N_2^r)^2 \sum_s y_s (N_3^s)^2
\]

\[
- \sum_r y_r (N_2^r)^2 \sum_s y_s (N_3^s)^2 = \sum_r \sum_s y_r y_s (N_2^r N_3^s - N_2^s N_3^r)^2
\]

\[ [A22] \]

holds only if \( N_2^r N_3^r - N_2^s N_3^s = 0 \) for all \( r \) and \( s \),

i.e. only if

\[
\beta_r = \frac{N_3^r}{N_2^r} = \frac{N_3^s}{N_2^s} = \beta_i \quad [A23]
\]

[A23] is just the same condition as eq. [62]

### Notation

**Symbols**

- \( c_i = N_i^r / N_i^t \)
- \( k \) = Boltzmann’s constant
- \( sc \) = solvent solution composition
- \( x = \text{mole fraction as in } x_i^r = N_i^r / \sum_i N_i^t + N_M \)
- \( \gamma_r = N_i^r / N_M = \text{fraction of } r \text{th micellar species } M \)
- \( \alpha = 1 - \beta \)
- \( \beta = \bar{N}_3 / \bar{N}_2 = \text{mean degree of counterion binding of micelles} \)
- \( \epsilon \) = subdivision potential of micelles
- \( \gamma = \text{activity coefficient} \)
- \( \mu \) = chemical potential

**Superscripts and subscripts**

\(-\) = as in \( N_i \) and \( \bar{N}_i \) refers to average property of micelles,

or as in \( \bar{V}_i \) refers to partial molecular property of monomeric species

\( \theta \) = as in \( \mu_i^0 \) refers to the reference state of monomeric species \( i \neq 1 \)

\( 0 \) = as in \( \mu_i^0 \) refers to a reference state of solvent water 1

\( i \) = refers to monomeric ionic species; 2, 3 and 4 referring respectively to surface active ion, counterion

and simili-ion

\( m \) = as in \( \mu_i^m \) refers to micellar state

\( M \) = as in \( \mu_i^M, \alpha_M \) and \( \gamma_M \) refers to properties of micelles

\( r \) = as in \( N_r \) and \( y_r \) refers to \( r \text{th micellar species } M \),

\( s \) = as in \( \mu_i^s \) refers to free solution

\( t \) = as in \( G_r, S_r \) and \( C_r \) refers to the total properties of micellar solution

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### References


12. M. TAMURA and M. TANAKA, Light Scattering and Surface Tension of Ionic Surfactant Solutions, (to be published).


