The Dependence of the Free Energy of Micelle Formation on Aggregation Number and Critical Micelle Concentration

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Abstract

It is shown that a formula proposed recently, to express the way in which the free energy of formation of molecular micelles depends upon the aggregation number of the micelles, is incorrect. The correct relationship is derived.

The mass action theory\(^4\) of the formation of micelles from neutral molecules \(A\) in solution supposes that monomeric species \(A\) exist in equilibrium with micellar aggregates \(A_n\) each containing a large and constant number \(n\) of monomer molecules:

\[
 nA_1 \rightleftharpoons A_n
\]  

(1)

If \(a\), \(a_1\) and \(a_n\) denote respectively the total concentration of \(A\), the concentration of \(A_1\) and the concentration of \(A_n\), and if the activity coefficients are assumed to be unity, the equilibrium and mass-balance conditions are

\[
 a/n = a_1^n = K
\]  

(2)

\[
 na_n + a_1 = a
\]  

(3)

The standard free energy change \(\Delta G^\circ\), per mole of monomer molecules, for the formation of micelles is therefore

\[
 \Delta G^\circ/RT = -(\ln K)/n = -(\ln a_1)/n + \ln(a - na_n)
\]  

(4)

The critical micelle concentration \(\text{CMC}\) can be defined\(^5\) as the value of \(a\) for which a plot of \(a_n\) against \(a\) has its maximum curvature, that is

\[
 a = \text{CMC} \quad \text{when} \quad d^3a_n/da^3 = 0
\]  

(5)

In order to derive \(\Delta G^\circ\) and its derivatives, the enthalpy and volume changes for micelle formation, from measurements of \(\text{CMC}\) alone, it is often assumed that (4) can

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be applied in the approximate form
\[ \Delta G^\circ/RT \approx \ln(\text{CMC}) \] (6)

where the terms involving \( a_n \) and \( n \) have been omitted.\(^7\) The justification for this simplification is not obvious and its use has recently been criticized by Birdi,\(^8\) who suggested that the temperature-dependence of the aggregation number \( n \) can make a significant contribution to the derivative \( \partial \Delta G^\circ / \partial T \). He rewrote (4) in a form equivalent to
\[ \Delta G^\circ/RT = -[\ln(na_n)]/n + (\ln n)/n + \ln(a-na_n) \] (7)

[the factor \( RT/N \) in his equations (7), (8), (12) and (13) should have been bracketed]\] and then proceeded, without explanation, to drop the term in \( \ln(na_n) \). He also replaced \( a-na_n \) by CMC, obtaining
\[ \Delta G^\circ/RT = (\ln n)/n + \ln(\text{CMC}) \] (8)

Since (8) involves two distinct and unrelated approximations, it would be a remarkable accident if it were correct. In point of fact, it is unnecessary to make any approximations at all. It is possible to eliminate \( a_n \) from (4) in an exact manner and obtain an expression for \( \Delta G^\circ \) in terms of just the two directly measurable quantities \( n \) and CMC. The method consists in solving the two simultaneous equations (4) and (5) for the two unknown quantities \( K \) and \( a_n \) by a method similar to one that Phillips\(^5\) applied to the formation of ionic micelles. The result is
\[ \Delta G^\circ/RT = \frac{1}{n} \ln \left[ \frac{n^2(2n-1)}{n-2} \right] + \frac{n-1}{n} \ln \left[ \frac{n(2n-1)}{(n-1)(2n+2)} \right] + \frac{n-1}{n} \ln(\text{CMC}) \] (9)

The monomer concentration at the critical micelle point is
\[ a_1 = \frac{n(2n-1)}{(n-1)(2n+2)} \times \text{CMC} \] (10)

the micelle concentration is
\[ a_n = \frac{n-2}{n(n-1)(2n+2)} \times \text{CMC} \] (11)

and their ratio is
\[ a_1/a_n = n^2(2n-1)/(n-2) \] (12)

If \( n > 50 \), then to a good approximation the second term in (9) can be neglected and, to a slightly less good one, the argument of the first term can be replaced by \( 2n^2 \), to give
\[ \Delta G^\circ/RT \approx (\ln 2 + 2 \ln n)/n + [(n-1)/n]\ln(\text{CMC}) \] (13)

To similar approximations
\[ a_1 \approx \text{CMC} \] (14)
\[ a_n \approx \text{CMC}/2n^2 \] (15)
\[ a_1/a_n \approx 2n^2 \] (16)

\(^7\) See, for example, Mukerjee, P., \textit{Adv. Colloid Interface Sci.}, 1967, 1, 241.

It will be seen that formula (8) bears little resemblance to the correct expression (9): it is also significantly different from the approximation (13). Table 1 shows the errors that result from the use of the several approximate relationships instead of (9). For the larger values of \( n \), the errors are small in comparison with the total value of \( \Delta G^0/RT \), which is about \(-5\) for the cases considered in Table 1. But for the smaller values of \( n \), the use of (8) or (6) instead of (9) or (13) may introduce errors of the order of 10%.

Table 1. Errors in the values of \( \Delta G^0/RT \) calculated from some approximate relationships

<table>
<thead>
<tr>
<th>Equation (9)</th>
<th>Equation (13)</th>
<th>Equation (8)</th>
<th>Equation (6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n = 10 )</td>
<td>+0.0199</td>
<td>-0.8095</td>
<td>-1.0397</td>
</tr>
<tr>
<td>( n = 20 )</td>
<td>+0.0177</td>
<td>-0.4317</td>
<td>-0.5815</td>
</tr>
<tr>
<td>( n = 100 )</td>
<td>+0.0047</td>
<td>-0.1012</td>
<td>-0.1473</td>
</tr>
<tr>
<td>( n = 500 )</td>
<td>+0.0010</td>
<td>-0.0234</td>
<td>-0.0359</td>
</tr>
</tbody>
</table>

The calculations have assumed a critical micelle concentration of \( \text{CMC} = 0.005 \text{ mol/dm}^3 \) throughout.

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