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[1-6] of the formation of micelles from neutral molecules A in solution supposes that monomeric species A_1 exist in equilibrium with micellar aggregates A_n each containing a large and constant number n of monomer molecules:

$$nA_1 \rightleftharpoons A_n \qquad (1)$$

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

$$a_n/a_1{}^n = K \qquad (2)$$

$$na_n + a_1 = a \qquad (3)$$

The standard free energy change ΔG°, per mole of monomer molecules, for the formation of micelles is therefore

$$\Delta G^\circ/RT = -(\ln K)/n = -(\ln a_n)/n + \ln(a - na_n) \qquad (4)$$

The critical micelle concentration 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

$$a = \text{CMC} \quad \text{when} \quad d^3 a_n/da^3 = 0 \qquad (5)$$

In order to derive ΔG° and its derivatives, the enthalpy and volume changes for micelle formation, from measurements of CMC alone, it is often assumed that (4) can

[1] Jones, E. R., and Bury, C. R., *Philos. Mag.*, 1927, **4**, 841.
[2] Murray, R. C., and Hartley, G. S., *Trans. Faraday Soc.*, 1935, **31**, 183.
[3] Corrin, M. L., *J. Colloid Sci.*, 1948, **3**, 333.
[4] Vold, M. J., *J. Colloid Sci.*, 1950, **5**, 506.
[5] Phillips, J. N., *Trans. Faraday Soc.*, 1955, **51**, 561.
[6] Mysels, K. J., *J. Colloid Sci.*, 1955, **10**, 507.

be applied in the *approximate* form

$$\Delta G^\circ / RT \approx \ln(\text{CMC}) \tag{6}$$

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

$$\Delta G^\circ / RT = -[\ln(na_n)]/n + (\ln n)/n + \ln(a - na_n) \tag{7}$$

[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

$$\Delta G^\circ / RT = (\ln n)/n + \ln(\text{CMC}) \tag{8}$$

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 ΔG° 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

$$\frac{\Delta G^\circ}{RT} = \frac{1}{n} \ln\left[\frac{n^2(2n-1)}{n-2}\right] + \frac{n-1}{n} \ln\left[\frac{n(2n-1)}{(n-1)(2n+2)}\right] + \frac{n-1}{n} \ln(\text{CMC}) \tag{9}$$

The monomer concentration at the critical micelle point is

$$a_1 = \frac{n(2n-1)}{(n-1)(2n+2)} \times \text{CMC} \tag{10}$$

the micelle concentration is

$$a_n = \frac{n-2}{n(n-1)(2n+2)} \times \text{CMC} \tag{11}$$

and their ratio is

$$a_1/a_n = n^2(2n-1)/(n-2) \tag{12}$$

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

$$\Delta G^\circ / RT \approx (\ln 2 + 2 \ln n)/n + [(n-1)/n]\ln(\text{CMC}) \tag{13}$$

To similar approximations

$$a_1 \approx \text{CMC} \tag{14}$$

$$a_n \approx \text{CMC}/2n^2 \tag{15}$$

$$a_1/a_n \approx 2n^2 \tag{16}$$

[7] See, for example, Mukerjee, P., *Adv. Colloid Interface Sci.*, 1967, **1**, 241.
[8] Birdi, K. S., in 'Colloidal Dispersions and Micellar Behaviour' (Ed. K. L. Mittal) p. 233, Am. Chem. Soc. Symp. Ser., Vol. 9 (American Chemical Society: Washington 1975).

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

Table 1. Errors in the values of $\Delta G°/RT$ calculated from some approximate relationships

The calculations have assumed a critical micelle concentration of CMC $= 0 \cdot 005$ mol/dm^3 throughout

	$n = 10$	$n = 20$	$n = 100$	$n = 500$
Equation (9)	0	0	0	0
Equation (13)	$+0 \cdot 0199$	$+0 \cdot 0177$	$+0 \cdot 0047$	$+0 \cdot 0010$
Equation (8)	$-0 \cdot 8095$	$-0 \cdot 4317$	$-0 \cdot 1012$	$-0 \cdot 0234$
Equation (6)	$-1 \cdot 0397$	$-0 \cdot 5815$	$-0 \cdot 1473$	$-0 \cdot 0359$

larger values of n, the errors are small in comparison with the total value of $\Delta G°/RT$, 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%.