2007, Volume 111B

Radina Hadgiivanova and Haim Diamant*: Premicellar Aggregation of Amphiphilic Molecules

Page 8854. In ref 1 we introduced a thermodynamic model for the micellization of amphiphilic molecules in solution, which allows one to study premicellar aggregation—i.e., the possible existence of metastable aggregates at concentrations well below the critical micelle concentration (cmc). We found that, *once thermodynamic equilibrium has been reached*, appreciable premicellar aggregation may occur for a finite concentration range below the cmc. The theory presented in ref 1, including that prediction, was based on equilibrium considerations related to free-energy differences between the monomeric and aggregated states. Those equilibrium results remain unchanged.

Toward the end of the paper (p 8858) we added an analysis of the free-energy barrier between the monomeric and aggregated states of the solution and derived the resulting nucleation barrier for the formation of a single micelle (eq 14 and Figure 7). There was an error in that last derivation. We got nucleation barriers of up to a few tens of k_BT (k_BT being the thermal energy), implying that a fully equilibrated partition between the stable monomeric and metastable aggregated states should be attained within the experimental time scales.

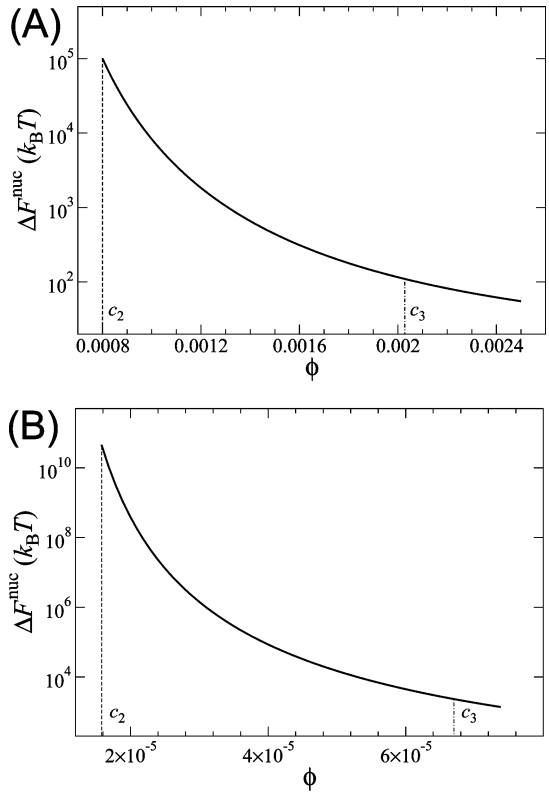

Figure 7. Nucleation barrier (in units of k_BT) as a function of total volume fraction. This figure corrects Figure 7 of ref 1. Panels A and B correspond to the parameters of the two exemplary amphiphiles treated in ref 1.

The error was in the transformation from the free-energy density (per unit volume), F/a^3, to the free energy per nucleus. In eq 14 we multiplied F/a^3 by $nm^{max}a^3/\phi$ (the volume of solution that contains the number of molecules m^{max} required to form a critical nucleus). (The volume of a single amphiphilic molecule is na^3, and the volume fraction of amphiphiles in the solution is ϕ.) That factor is much too small. The correct volume, by which the free-energy density should be multiplied, is the subvolume of solution that contains, on average, one aggregate of critical size, $nm^{max}a^3/\phi_m$, where $\phi_m = \phi - \phi_1$ is the volume fraction of aggregates and ϕ_1 the volume fraction of monomers.[2] Thus, eq 14 should be corrected to

$$\Delta F^{nuc}(\phi) = \frac{nm^{max}}{\phi - \phi_1^{min}(m^{max})}[F(\phi_1^{min}(m^{max}),m^{max},\phi) - F(\phi_1^{min}(m=1),m=1,\phi)] \quad (14)$$

Since $\phi_m = \phi - \phi_1 \ll \phi$ in the dilute premicellar regime, this correction makes a big difference. As is seen in the corrected Figure 7, the resulting nucleation barriers for the two examples treated in ref 1 are extremely high. Still high but physically surmountable free-energy barriers on the order of 10^2 k_BT are obtained only for the case of the less hydrophobic amphiphile at concentrations around the cmc c_3 (Figure 7A).

The conclusion from this correction is that the homogeneous nucleation of premicellar aggregates in pure solutions is kinetically hindered and is not expected to occur within reasonable experimental time limits. Nonetheless, the presence of a third component, acting as a nucleation center, might significantly lower the barrier and enable premicellar aggregation. This suggests a possible resolution for the long-standing controversy concerning premicellar aggregation. The possible large extent of the phenomenon in fully equilibrated solutions, on the one hand, and the high kinetic barriers in pure systems, on the other hand, may explain why premicelles have been observed in solutions containing a very low concentration of an amphiphilic impurity (e.g., in fluorescence correlation and other spectroscopic techniques involving amphiphilic probes; see references in ref 1) and not in pure solutions (using, e.g., highly sensitive conductivity measurements). Thus, the premicelles observed in certain experiments may be genuine, in the sense that the impurity present in such experiments does not necessarily lower the cmc for the formation of stable micelles but rather facilitates the nucleation of (the otherwise kinetically hindered) metastable micelles.

References and Notes

(1) Hadgiivanova, R.; Diamant, H. *J. Phys. Chem. B* **2007**, *111*, 8854–8859.

(2) Hadgiivanova, R.; Diamant, H. *J. Chem. Phys.* **2009**, *130*, 114901.

10.1021/jp102926b
Published on Web 04/29/2010