Platonic micelles: A new concept of micelles since their discovery 100 years ago

Surfactants and lipids comprise hydrophilic polar headgroups and hydrophobic tails, which are commonly long hydrocarbon chains. When these molecules are dispersed in aqueous solutions, the hydrophobic tails tend to avoid unfavorable interactions with polar water, while the headgroups favorably interact with water. This consequently leads to the formation of aggregates with a certain size called "micelles." This term was first used by J. W. McBain in 1913 to describe an aggregate of soap molecules, and the first model of spherical micelles was proposed by G. S. Hartley [1]. In Hartley's micelle model, the polar headgroups usually form the exterior of the aggregate and the hydrophobic moieties form the interior.

Tanford was the first to formulate the thermodynamics of micelle formation [2]. His theory and its improvements, and also recent computer simulations based on these theories are reasonably consistent with various experimental results for a wide range of materials. It is generally accepted that the aggregation number (N_{agg}) gradually changes with the surfactant concentration and other solvent conditions such as the ionic strength and that N_{agg} has a certain distribution. However, we recently observed an interesting phenomenon that seemingly cannot be rationalized within the above framework.

We have newly synthesized calix[4]arene-based amphiphiles, all of which consist of four headgroups and four alkyl tails and have a conical shape, as presented in Fig. 1(a). Synchrotron small angle X-ray scattering (SAXS) measurement was carried out at SPring-8 **BL40B2** to determine the micelle shape composed of the amphiphile as well as the N_{agg}.

We first identified that a calix[4]arene-based amphiphile bearing amines and propyl chains forms hexamer micelles at pH = 3 without any distribution in N_{agg} [3]. We also found that some calix[4]arene-based amphiphiles self-assemble into spherical micelles exhibiting similar monodispersity of N_{agg}. The monodispersed aggregation numbers that we have so far identified are 4, 6, 8, 12, 20. It is quite surprising that those numbers coincide with the vertex numbers of regular polyhedral structures, i.e., Platonic solids, as illustrated in Fig. 1(a), and we name them "Platonic micelles." The monodispersity and discreteness of N_{agg} have been found in another micellar system composed of surfactin, which consists of a heptapeptide unit (Glu-Leu-D-LeulVal-Asp-D-Leu-Leu) and a beta-hydroxy fatty acid. The present results indicate that a suitable combination of amphiphile tail length, head volume, and sufficiently small N_{agg}, as well as some rigidity of the building block, is necessary to produce Platonic micelles, which are monodisperse with a defined N_{agg} whose values are chosen from the vertex numbers of regular polyhedra [4].

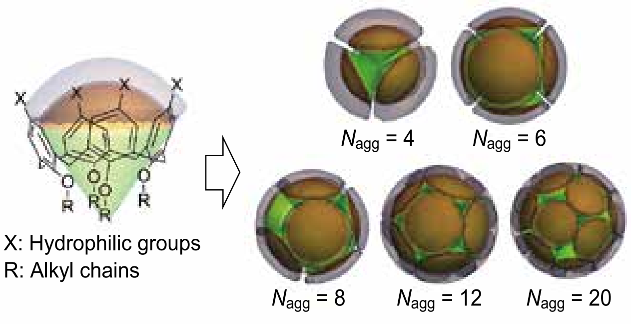

Fig. 1. Chemical structure of a calix[4]arene-based amphiphile and schematic illustration of calix[4]arene-based micelles whose N_{agg} values match the vertex numbers of regular polyhedra.

There have been no reports of such discreteness and monodispersity in conventional micelles. Generally, normal micelles have larger N_{agg} values than the present systems. If the interfacial area (a_e) between a hydrophilic domain and a hydrophobic domain is large and N_{agg} is small, the way in which the hydrophobic tails are covered to achieve the minimum free energy may differ from the systems with a large N_{agg}. This issue is probably related to the mathematical problem of how to efficiently cover a spherical surface with multiple identical spherical caps. In geometry, this is called the "best packing on a sphere" or the Tammes problem. For example, as illustrated in the right of Fig. 2(a), the maximum coverage with three spherical caps is $D(N) = 0.75$. For 12 caps (left of Fig. 2(a)), we can have a larger coverage of $D(N) = 0.90$ and the centers of the caps have the same configuration as the vertices of a regular icosahedron. Here, $D(N)$ is defined as the ratio of the sum of the cap areas to the area of the sphere surface.

Figure 2(b) plots $D(N)$ against the number of caps N. For small N, larger $D(N)$ values are obtained at certain numbers such as N = 4, 6,12, and 20. It is surprising that these numbers coincide with our observed values of N_{agg}. In an analogy to the above, it can be reasonably assumed that there are certain

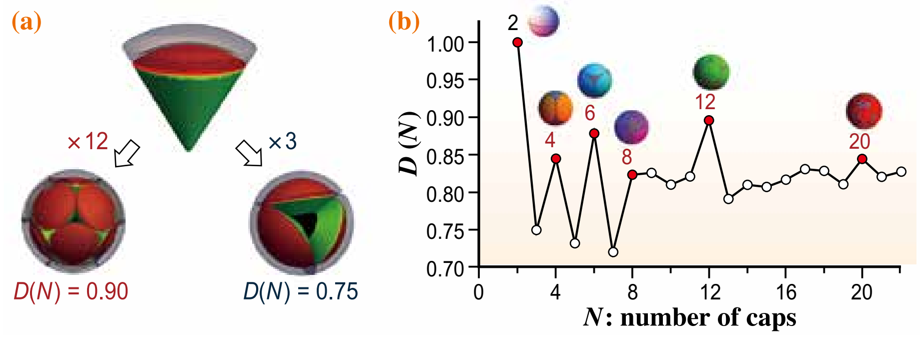

Fig. 2. **(a)** Two examples of the best packing of multiple circles on a sphere surface (N = 3 and 12). The Tammes problem and its analogy of how multiple cone-shaped surfactants form spherical micelles to cover their hydrophobic tail domain (green) with the interface area (red) acting as spherical caps. **(b)** Coverage $D(N)$ of the Tammes problem plotted against the number of caps N.

numbers of molecules that can more efficiently cover spherical micelles than other numbers. One may think that real molecules do not behave like rigid spherical caps, but the hard-core potential (i.e., Tammes problem) is not a necessary condition for an oscillating $D(N)$ pattern. A similar simulation with the Coulomb potential exhibits local maxima at the same values of N as those in the Tammes problem. Therefore, we can presume that N_{agg} = 4, 6,12, and 20 are more likely to be encountered in real micelles. The monodispersity can be explained in the same framework. When a certain N_{agg} is strongly favorable, most aggregates will consist of this number of molecules and the system becomes monodisperse.

We have also observed a very interesting kinetic transition from calix[4]arene-based dodecamer micelles to icosamer ones when increasing the salt concentration (Fig. 3(a)) [5]. N_{agg} remained unchanged during the first 60 s after the increase in NaCl concentration, and then abruptly increased to 20 (Fig. 3(b)). We surmise that this phenomenon is probably due to the fact that only a few N_{agg} values are thermodynamically allowed in the system of Platonic micelles.

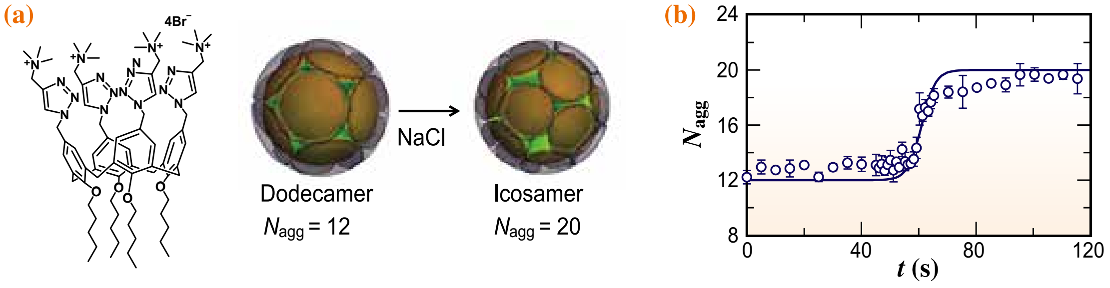

Fig. 3. **(a)** Chemical structure of the calix[4]arene-based amphiphile bearing quaternary amines and schematic illustration of the salt-induced transition of the micelles from dodecamer to icosamer. **(b)** Time evolution of N_{agg} (circles) and the fitting curve.

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