Binary-component micelle and vesicle: Free energy and asymmetric distributions of amphiphiles between vesicle monolayers

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The real-space two-dimensional self-consistent field theory (SCFT) is employed to study the free energies of micelles and vesicles constituted by binary amphiphilic diblock copolymer AB in homopolymer A. With an increasing volume fraction of copolymer AB, there are morphological transitions from circle micelles to oblate circle-like micelles, to a compound structure with inverted micelles in the inner center and micelles outer layer, and to vesicles. Special attention is paid to the role of the copolymer AB in controlling the free energies of the micelles and vesicles by examining the effect of the length ratio of A/B with the fixed whole chain length of the AB copolymer, the length effect of A or B block with the corresponding fixed length of B or A block, for one component of copolymer, and the effect of different amphiphile compositions for a binary-component copolymer system. The quantity η is provided to describe the asymmetric density distribution of amphiphiles between the inner and outer monolayers of vesicles, and to quantify the relative asymmetric extent of the density distribution between two species of copolymers in binary component vesicles.

Keywords: binary components, vesicle, micelle, asymmetry distribution

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1. Introduction

As biological membranes are very complex systems,[1–4] many model membranes have been developed for studying membrane properties, structures, and processes, as well as for investigating the membrane activity of diverse natural or synthetic compounds such as surfactants, peptides, and drugs. The most well-known and common biomimetic systems used for such purposes are lipid monolayers, lipid vesicles, and supported lipid bilayers,[5] as well as copolymer micelles, copolymer vesicles, and copolymer bilayers.

Vesicles prepared using amphiphilic block copolymers (also called polymersomes[6–11]) are of potential interest for a number of applications including drug delivery and controlled release. Compared with vesicles prepared with conventional small-molecule surfactants, polymer-based systems are more robust, have thicker walls (providing a greater barrier to diffusion), and can be prepared using tailored polymer chemistries with tunable physiochemical properties. Furthermore, there are many experimental investigations on the vesicle formation in binary amphiphilic block copolymer/homopolymer systems.[12,13]

Recently, increasing attention has been paid to the multicomponent membrane vesicles of binary and/or ternary lipid mixtures, because these systems are simpler model systems for understanding the behavior of real biomembranes, which are intrinsically composed of many kinds of lipids and membrane proteins. Most of these works are concerned with the shape deformations of binary giant unilamellar vesicles (GUVs) composed of cone- and cylinder-shaped lipids,[14,15] phase separations and the corresponding morphological evolutions of vesicles,[16–24] budding of multicomponent membrane vesicles,[25–27] fusion, and fission dynamics of vesicles.[15,28–31] A common issue is the effect of different head/tail length ratios on the stability of micelles and vesicles. For vesicles, the curvatures of the inner and outer monolayers are different, which accommodate specific type of lipids. However, the dependence of the free energies of vesicles on amphiphile structural parameters, such as the copolymer chain length, the head/tail length ratio, and compositions, have not been systematically studied.

Generally, the components of biological membranes are asymmetrically distributed between two surfaces.[14,32,33] Almost every type of lipid is present on both sides of membrane bilayers, but with different amounts. Most biological membranes appear to have different phospholipid compositions in their inner and outer leaflets. This asymmetrical distribution is believed to facilitate the flip of the lipids in one leaflet of the bilayer.[34] The distribution details of lipids in planar bilayers have been well characterized. For curved bilayers, such as vesicles, however, little data is available.[35]

Using a self-consistent field theory (SCFT),[36–38] the aim of the present work is mainly to investigate the effect of amphiphile composition on the free energies of micelles and vesicles, in which the mixing ratios of amphiphile components vary for a binary-component copolymer system. The lipid molecule is molded as the AB copolymer with blocks A and B corresponding to the head (h) and tail (t) portions of the lipid. Homopolymer A is used as a solvent (s) molecule. The binary-component system consists of two copolymer species, which are represented by the same type of copolymer AB. The two species are different in A and B block lengths, or different

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in lengths of the whole copolymer chain under the same A/B length ratio. Here we especially focus on the effects of total chain length and different head/tail length ratios at the same chain length, different total chain lengths at fixed head/tail length ratio, and different head or tail lengths for fixed tail or head length, respectively. Based on the understanding of these effects, we will investigate the asymmetric distributions of copolymers between the inner and outer monolayers of vesicles, and analyze which type of copolymer has the relative priority to be located in the outer or inner monolayer of the binary-component vesicle.

2. Model of a two-component vesicle and micelle

The self-consistent field theory is used to study the formation of micelles and vesicles in a solution of an incompressible copolymer-homopolymer mixture. The system consists of n_a linear amphiphilic copolymers and n_s solvent molecules. The amphiphilic molecules are composed of A (hydrophilic) and B (hydrophobic) monomers, and the solvent molecules are represented by hydrophilic homopolymers consisting of A segments only. Each homopolymer chain consists of N segments with a fixed monomer volume $1/\rho_0$, with each copolymer chain consisting of αN segments with the same volume $1/\rho_0$. We assume that the A and B segments have the same segment length b. The dimensionless free energy of the system is given by[36–39]

$$\begin{aligned}
&\frac{NF}{\rho_0 k_B T V} \\
&= -\frac{\bar{\phi}_a}{\alpha}\ln\left(\frac{Q_a}{V\bar{\phi}_a}\right) - \bar{\phi}_s \ln\left(\frac{Q_s}{V\bar{\phi}_s}\right) \\
&\quad + \frac{1}{V}\int \mathrm{d}\boldsymbol{r}[\chi N\phi_h(\boldsymbol{r})\phi_t(\boldsymbol{r}) + \chi N\phi_s(\boldsymbol{r})\phi_t(\boldsymbol{r})] \\
&\quad - \frac{1}{V}\int \mathrm{d}\boldsymbol{r}[w_h(\boldsymbol{r})\phi_h(\boldsymbol{r}) + w_t(\boldsymbol{r})\phi_t(\boldsymbol{r}) + w_s(\boldsymbol{r})\phi_s(\boldsymbol{r})] \\
&\quad + \frac{1}{V}\int \mathrm{d}\boldsymbol{r}\xi(\boldsymbol{r})[\phi_h(\boldsymbol{r}) + \phi_t(\boldsymbol{r}) + \phi_s(\boldsymbol{r}) - 1]. \qquad (1)
\end{aligned}$$

Here, the local volume fractions of A (head) and B (tail) segments of the amphiphiles are given by $\phi_h(\boldsymbol{r})$ and $\phi_t(\boldsymbol{r})$. Likewise, $\phi_s(\boldsymbol{r})$ is the local concentration of homopolymer solvent. The average volume fractions of amphiphilic copolymer and solvent homopolymer are $\bar{\phi}_a$ and $\bar{\phi}_s$, respectively. The $w_h(\boldsymbol{r})$, $w_t(\boldsymbol{r})$, and $w_s(\boldsymbol{r})$ are the conjugate fields to the local volume fractions $\phi_h(\boldsymbol{r})$, $\phi_t(\boldsymbol{r})$, and $\phi_s(\boldsymbol{r})$, respectively, in a space point $\boldsymbol{r}$. The k_B is the Boltzmann constant, and T is the absolute temperature. The hydrophobic and hydrophilic monomers interact with a local Flory–Huggins interaction repulsion parameter of strength χ, with a choice $\chi N = 30$. The $\xi(\boldsymbol{r})$ is the Lagrange multiplier which enforces the incompressibility condition of the system. The Q_s and Q_a are the single chain partition functions of the solvent and amphiphile molecules subjected to the above fields. V is the total volume of the system.

To form the starting configuration, an equilibrated spherical "micelle" or "vesicle" is created by using an artificially "biased" structure.[40–43] The periodic boundary conditions are exploited in our calculations. For clarity, all the figures of micelles and vesicles in the paper are cut from the whole system, whose size is $200 \times 200\ R_g$. The R_g is the gyration radius of the homopolymer chains.

3. Results

We first focus on the influences of the average volume fraction of the AB copolymer on the free energies and structures of micelles and vesicles. For a copolymer AB and homopolymer A system, Fig. 1 shows the morphological transformations with an increasing amount of copolymer AB. It forms a circle micelle when $\bar{\phi}_a = 0.06$ and an oblate micelle when $\bar{\phi}_a = 0.08$ and 0.09. When $\bar{\phi}_a = 0.1$, a composite structure appears with an inverted micelle in the core surrounded by a circle micelle in the outer layer. When $\bar{\phi}_a$ increases enough, to 0.4, a circle vesicle appears. Obviously, the free energies corresponding to these structures increase with the increment in $\bar{\phi}_a$, as shown in the bottom figure of Fig. 1. These results somewhat correspond to the pathway of the micelles growth by attracting copolymers from the solution to a critical micelle size, where the micelle core becomes solvent-philic (semi-vesicle state). Finally, solvent molecules diffuse into the core, and the semi-vesicle swells into a vesicle.[44,45]

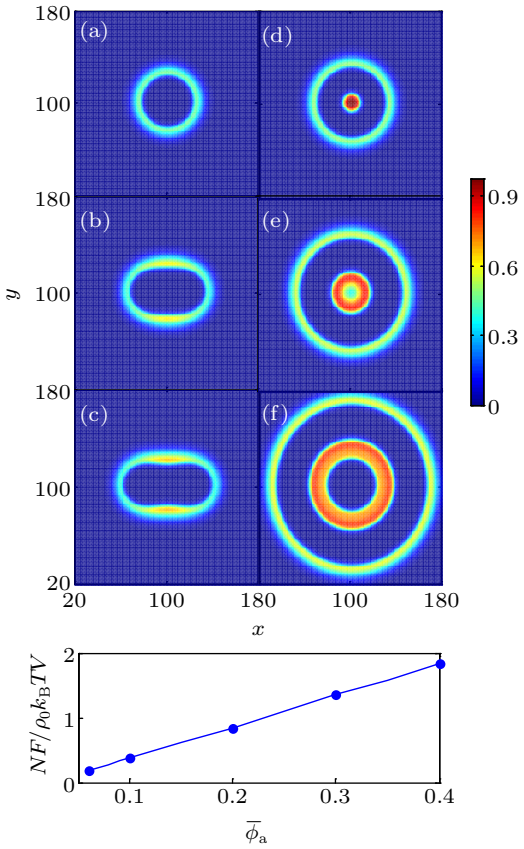


Fig. 1. (color online) Density distributions of block A, ϕ_h, with the copolymer concentration being (a) $\bar{\phi}_a = 0.06$, (b) 0.08, (c) 0.09, (d) 0.1, (e) 0.2, and (f) 0.4 for a single-component polymeric membrane with $N_h/N_t = 30/70$ and $N = 100$. The corresponding free energy as a function of the diblock volume fraction $\bar{\phi}_a$ is shown in the bottom figure.

To clearly analyze the multicomponent effect, only the total length of copolymer or the ratio of hydrophilic/hydrophobic length is changed. For convenience, we define $\gamma = N_h/N_t$, where $\gamma > 1$ means a long head with a short tail, or vice versa. We will explore the effect of γ on the free energies of micelles and vesicles from two aspects.

First of all, we fixed the head length or tail length, and changed the length of the tail or head, respectively. Figure 2 shows the influences of different tail or head lengths on the free energies of micelles and vesicles for the head length or tail length fixed at 80. Both figures show similar behavior. When comparing the head length with the tail length in the same copolymer chain, the copolymer with a longer head and a shorter tail prefers to constitute micelles and vesicles.

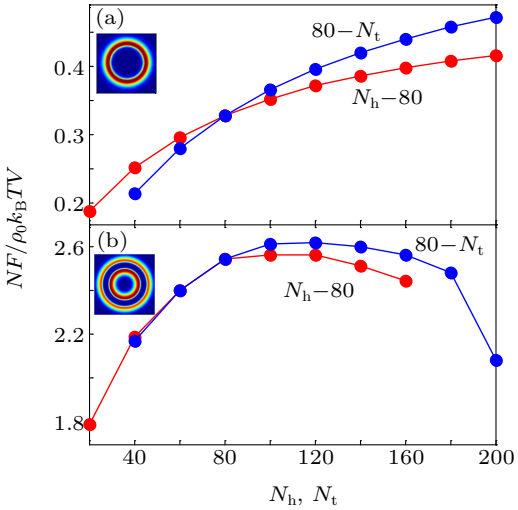


Fig. 2. (color online) The free energies of (a) micelles and (b) vesicles as functions of the hydrophilic length for fixed hydrophobic length $N_t = 80$ (red line) and the hydrophobic length for fixed hydrophilic length $N_h = 80$ (blue line). All these curves are calculated at copolymer volume fraction $\bar{\phi}_a = 0.06$ for micelles and $\bar{\phi}_a = 0.4$ for vesicles.

Next, we fixed the whole chain length of the copolymer, and changed the head/tail length ratio. Figure 3 shows the free energies of micelles and vesicles as functions of γ for $N = 100, 160, 200$, and 300. It can be seen from the decreasing free energy curves that the micelles always favor the amphiphiles with a long head and a short tail. It is interesting that for the vesicle there is a maximum in the free-energy curve at $\gamma = 1$ for the copolymer whose total chain length is longer than the solvent length. For the same amphiphile molecules, there is competition between the inner monolayer and outer monolayer, because the curvatures of the two leaflets of the vesicle are opposite to each other. The heads of the amphiphiles are oriented toward the solvent core in the inner monolayer and toward the outer shell in the outer monolayer. This is also clearly reflected in the conformational entropy of the copolymer chains in Fig. 3(c) for $N = 300$, which is given by[46,47]

$$\frac{NS}{\rho_0 k_B TV} = \frac{1}{V}\int d\boldsymbol{r}[w_h(\boldsymbol{r})\phi_h(\boldsymbol{r}) + w_t(\boldsymbol{r})\phi_t(\boldsymbol{r})] - \frac{\bar{\phi}_a}{\alpha}\ln\left(\frac{V\bar{\phi}_a}{Q_a}\right). \quad (2)$$

From this entropy formula, we can obtain the conformational entropies of the inner and outer monolayers, respectively. Both the inner and outer monolayers show the maximal entropies when the head length equals the tail length. Otherwise, the entropies are smaller when $\gamma \neq 1$.

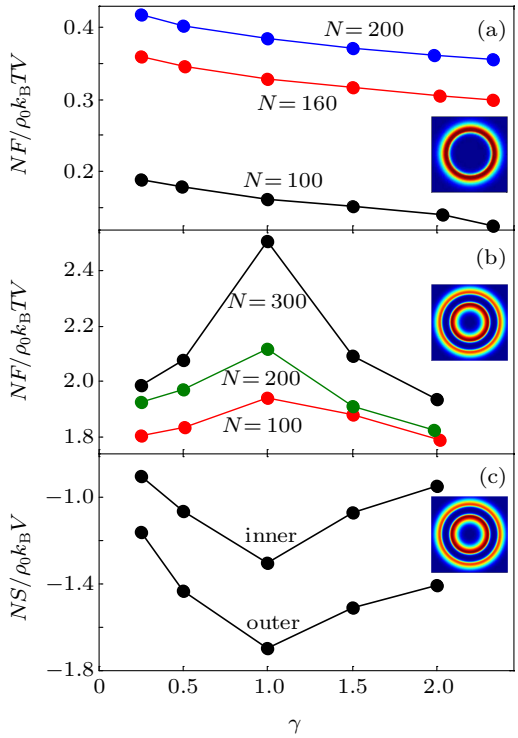


Fig. 3. (color online) The free energies of (a) micelles and (b) vesicles as functions of γ at fixed copolymer chain length $N = 100$, 160, 200, and 300, respectively. All these curves are calculated at copolymer volume fraction $\bar{\phi}_a = 0.06$ for micelles and $\bar{\phi}_a = 0.4$ for vesicles. (c) Conformational entropies of the inner and outer monolayers at different γ for the vesicle in (b) with $N = 300$.

For binary-component micelles and vesicles, figure 4 shows their free energies as functions of average volume fractions of two copolymer species, which are different in total chain lengths and head/tail ratios. It is noted that the micelle formed only by a 60/40 component has smaller free energy than that by a 40/60 copolymer, as shown in Fig. 3(a). However, if the two components together constitute micelles, the free energies reach the minimal values at $\phi = 0.03$, smaller than that of the micelles formed solely by one of the two species, as shown in Fig. 4(a). From the curvature point of view, the inner leaflet of the vesicle prefers to accommodate a copolymer with a short head and a long tail, while the outer leaflet likes a copolymer with a long head and a short tail. Thus, the vesicle comprised of two species of copolymers, such as 60/40 and 40/60, has a minimal value in the free energy curve, as shown in Fig. 4(b).

In the binary system, there is a clear tendency toward partial demixing of the two components, with one component enriched in one monolayer. Figure 5 shows a binary-component vesicle. A small difference in copolymer composition between the inner and outer monolayers is found, with more 90/30 component copolymer populating in outer monolayer than the

inner monolayer, and more 30/30 copolymer locating in the inner monolayer than the outer monolayer. Compared with the 30/30 copolymer molecule, the 90/30 copolymer is a cone-shaped molecule characterized by a negative spontaneous curvature. This observation is in line with the simple packing argument that the outer monolayer prefers cone-shaped lipids such as the 90/30 copolymer molecular here.

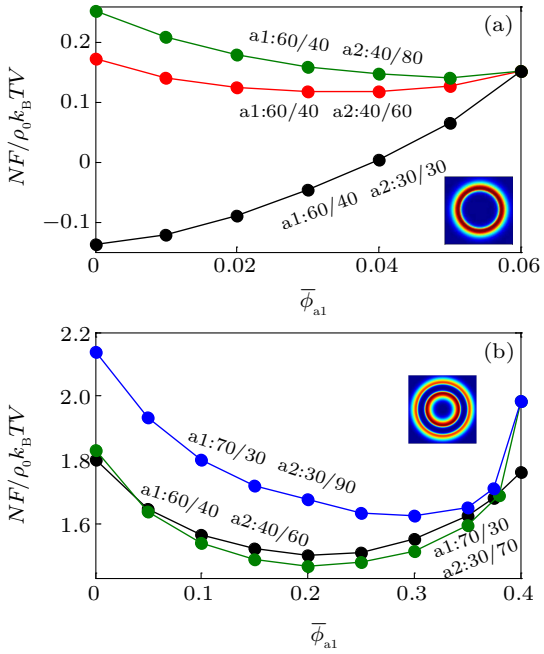


Fig. 4. (color online) (a) The free energies of binary-component micelles as functions of $\bar{\phi}_{a1}$ at fixed $\bar{\phi}_a = 0.06$ for different combinations of two components. Here, the a1 copolymer has a block length of $N_h/N_t = 60/40$, the a2 copolymers have different ratios of N_h/N_t =40/80, 40/60, 30/30. (b) The free energies of the binary-component vesicles as functions of $\bar{\phi}_{a1}$ at fixed $\bar{\phi}_a = 0.4$ for different combinations of two components. Here, the a1 copolymers have block lengths of N_h/N_t =70/30 and 60/40, the a2 copolymers have different lengths of N_h/N_t =30/90, 40/60 and 30/70.

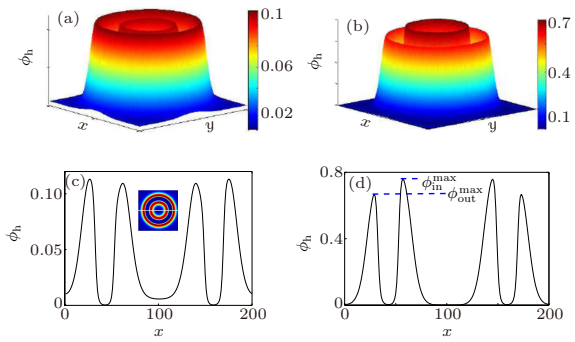


Fig. 5. (color online) Density distributions of each constituent of the binary-component vesicle in the *xy* space (top figures) and along the intercepting line through the center of the vesicle (bottom figures). The parameters of the two-component amphiphiles are N_h/N_t =90/30 and $\bar{\phi}_{a1} = 0.05$ for copolymer a1, N_h/N_t =30/30 and $\bar{\phi}_{a2} = 0.35$ for copolymer a2.

To quantify the asymmetry extent of the density of the copolymer in the inner and outer monolayers, we define a density asymmetry quantity as

$$\eta = (\phi_{in}^{max} - \phi_{out}^{max})/(\phi_{in}^{max} + \phi_{out}^{max}), \quad (3)$$

where ϕ_{in}^{max} and ϕ_{out}^{max} are the maximal densities of the head part of copolymer in the inner and outer leaflets, as shown in Fig. 5, and $|\eta|$ ranges from zero for symmetry distribution to one for distribution only in one leaflet. Positive η means higher density in the inner monolayer than that in the outer monolayer. On the contrary, negative η denotes a higher density in the outer monolayer than that in the inner one.

Figure 6 shows η as a function of the average volume fractions, $\bar{\phi}_{a1}$, under the fixed total volume fraction of amphiphiles, for different binary-component vesicles. Obviously, a larger γ is needed when $\gamma > 1$ for the vesicle with higher density in the outer monolayer than that in the inner monolayer.

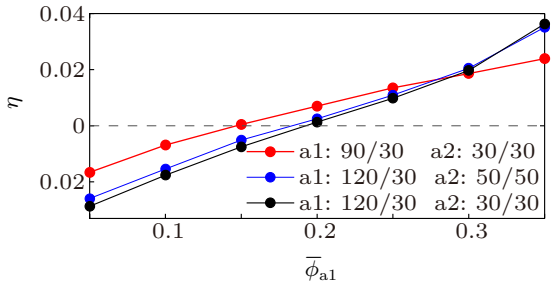


Fig. 6. (color online) Binary-component vesicles with different combinations of two components: I, a1: 90/30, a2: 30/30; II, a1: 120/30, a2: 30/30; III, a1: 120/30, a2: 50/50. The figure shows the density asymmetric extent for a1 component, η_{a1}, as a function of volume fractions of a1 copolymer component at fixed $\bar{\phi}_a = 0.4$.

Physically, we can identify which copolymer has the priority to distribute in the inner monolayer, depending on the value of η. It should be calculated when the two components have the same average volume fraction. For example, in binary mixture $(90/30) : (30/30)$ with $\bar{\phi}_{90/30} = \bar{\phi}_{30/30} = 0.2$, $\eta_{90/30} = 0.007$, and $\eta_{30/30} = 0.0811$, the latter is larger than the former, which means that the 30/30 component prefers to be located in the inner monolayer more than the 90/30 does.

Generally speaking, the larger γ components prefer to be located in the outer leaflet. If $\gamma > 1$ for both the components, the component with larger γ has the priority to lie in the outer monolayer. For example, for the vesicle formed by copolymers, if N_h/N_t corresponds to 90/30, $\eta_{90/30} = 0.0106$; if N_h/N_t corresponds to 70/50, $\eta_{70/50} = 0.0618$. The concentration of the 90/30 copolymer is higher than that of 70/50 copolymer in the outer monolayer, i.e., the 90/30 copolymers have a relatively strong tendency to occupy the outer monolayer. If $\gamma < 1$ for both the two components, for instance, the 30/70 and 40/60 binary vesicle, $\eta_{30/70} = 0.1065$, and $\eta_{40/60} = 0.0694$. The 30/70 component has the relative priority to lie in the inner monolayer. The effects of different total chain lengths on the asymmetric distributions between two monolayers can also be explained by the comparisons of η.

This priority of distribution in the inner or outer monolayer is relative. The relative preference for one type of copolymer to be in the outer monolayer is also described by η. For a vesicle constituted by 30/70 copolymer and 50/50 copolymer, $\eta_{30/70} = 0.1128$, $\eta_{50/50} = 0.049$, and the 50/50 copolymer prefers to be in the outer monolayer; while for a vesicle formed by 120/30 copolymer and 50/50 copolymer,

$\eta_{120/30} = 0.0025$, $\eta_{50/50} = 0.0997$, and the 50/50 copolymer prefers to be in the inner monolayer.

These asymmetric distributions between the inner and outer monolayers are qualitatively similar to that for the lipids. Based on the shape model of lipids, the inner monolayer should clearly favor for the inverted-cone shaped lipids (for example, DPPE and DLiPC).[48] It is somewhat a limitation to analyze this asymmetric density distribution between two monolayers under the framework of the SCFT, compared to the real lipid vesicle environment. We will resort to the molecular dynamics simulations to further explain this asymmetric distribution phenomenon.

4. Conclusions

We have investigated thoroughly the influences of the hydrophilic and hydrophobic block lengths of the amphiphile molecules on the free energies of micelles and vesicles by means of different hydrophilic (or hydrophobic) block lengths at fixed hydrophobic (or hydrophilic) lengths and different ratios of hydrophilic lengths to hydrophobic lengths at fixed amphiphile lengths. Our research is related to different types of lipids: cone shapes or inverted-cone shapes. We have also explored a simple two-component amphiphile system to explain the multicomponent effect on the free energies of micelles and vesicles, and to analyze the asymmetric distribution of amphiphile molecules between the inner and outer monolayers of vesicles.

For one type of copolymer, an obvious asymmetric structure exists between the inner and outer leaflets of the vesicle within the self-consistent field theory. The asymmetry of density distribution between the two monolayers has been studied by analyzing η. Also, we can identify which type of copolymer has the priority to live in the inner or outer monolayer by comparing η of different amphiphiles in multicomponent vesicles. These asymmetric structures for different types of amphiphiles are believed to be related to fusion and fission of vesicles and budding and budding off of multicomponent membrane vesicles.[15,25,31]

The morphology and fusion (fission) of multi-component vesicles based on these results are currently underway.

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