

# Molecular Packing Parameter in Bolaamphiphile Solutions: Adjustment of Aggregate Morphology by Modifying the Solution Conditions

Yun Yan,<sup>†</sup> Wei Xiong,<sup>†</sup> Xiaosong Li,<sup>†</sup> Ting Lu,<sup>†</sup> Jianbin Huang,<sup>\*,†</sup> Zichen Li,<sup>\*,†</sup> and Honglan Fu<sup>‡</sup>

State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, and College of Life Science, Peking University, Beijing, 100871, People's Republic of China

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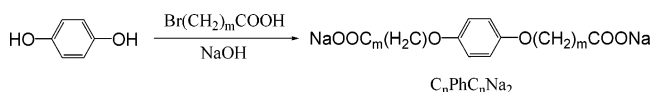
The geometrical rule of molecular packing parameters in a bolaamphiphile solution was tested with experimental results. By modifying the solution conditions to change the molecular packing parameters, the morphology of the aggregate was successfully manipulated in a single-chain bolaamphiphile, disodium phenyl-1,4-bis(oxyhexanoate) (i.e., C<sub>6</sub>PhC<sub>6</sub>Na<sub>2</sub> solution). Micelle–vesicle–tube transformation was observed by changing the pH and the addition of NaBr or octanol. In the mixed systems of oppositely charged bola/surfactants, the molecular packing parameter's role is related to the mixing ratio.

## Introduction

The molecular packing parameter  $P$  was a concept developed by Israelachvili et al. to explain, rationalize, and even predict the shape of molecular self-assembled structures in conventional surfactant solutions.<sup>1</sup> The molecular packing parameter is defined as  $P = v_0/al_0$ , where  $v_0$  and  $l_0$  are the volume and length of the surfactant hydrophobic tail and  $a$  is the area of the surfactant head group at the interface of the hydrophobic core–hydrophilic media. In the last two decades, the packing parameter has been widely cited in chemistry, physics, and biology research because it allows a simple and intuitive insight into the relationship between molecular structures and the shape of self-assembly. For example,  $0 < P \leq 1/3$  is for spherical micelles,  $1/3 < P \leq 1/2$  is for cylindrical ones, and  $1/2 < P \leq 1$  is for bilayer structures, such as vesicles.

The molecular packing parameter also indicates a way to realize the aggregate morphology transition by changing the solution conditions.<sup>2</sup> For a given surfactant,  $v_0/l_0$  is fixed since both  $v_0$  and  $l_0$  are the nature of the molecule. However,  $a$  can be changed by modifying the solution conditions because  $a$  is influenced directly by the head group interactions. For example, adding salt to an ionic surfactant solution decreases  $a$  due to a decrease in ionic repulsions, which results in an increase of  $v_0/al_0$ . Therefore, the spherical micelle is transformed into a rod-like one and possibly to vesicles by modifying the solution conditions. The molecular packing theory agrees well with numerous results on the conventional surfactant systems,<sup>3–6</sup> and it was also successfully applied to a novel amphiphile system, such as the bolaamphiphile (bolas) solution by Nagarajan, where the packing arguments are systematically developed and the thermodynamics of bolaamphiphile aggregation has been fully treated.<sup>7</sup> However, in his work, Nagarajan did not discuss cylindrical bilayers but combined all bilayers (spherical, tube-like, or planar) into one category within the broad packing parameter range from 0.5 to 1. Therefore, it will be necessary

## SCHEME 1: Bolaamphiphiles C<sub>n</sub>PhC<sub>n</sub>Na<sub>2</sub> ( $n = 6, 10; m = n - 1$ )



to further group the three geometries based on the packing considerations.

Bolaamphiphiles are molecules with two polar head groups at each end of the hydrophobic chain.<sup>8</sup> Instead of the formation of a double molecular layer, they can self-assemble into monolayers on a solid surface or in solutions.<sup>9–12</sup> However, the basic thermodynamic properties of bolas, such as CMC and micellization free energy, are not simply twice that of the corresponding conventional surfactant with a half length. For instance, the CMC of an eicosanediyl 1,20-bis(pyridinium bromide)(C<sub>20</sub>-Py<sub>2</sub>) solution is nearly 2 orders less than that of decylpyridinium bromide (C<sub>10</sub>Py),<sup>13</sup> whereas the micellization entropy and enthalpy of the former are about 5 times more than that of the latter.<sup>13,14</sup> We also found that vesicles were spontaneously formed in a mixed system of bola/conventional surfactant.<sup>15,16</sup> In proper situations, the vesicles may transform into tubes or elongate aggregates.<sup>17–19</sup> Indeed, large variety of self-assemblies, including micelles, vesicles, tubes, and fibers, are found so far in aqueous solutions of different bolaamphiphiles,<sup>20–24</sup> but few efforts were made on understanding the molecular packing theory in these systems as compared to what has been done in conventional surfactant solutions. Therefore, in this study, we hope to contribute some general knowledge on the role of molecular packing parameters in the solutions of bolaamphiphiles, especially the role they play in the process among spherical, tube-like, and planar bilayer structures. The general rules of molecular packing parameters for symmetric bola molecules are applied to a bolaamphiphile, the disodium phenyl-1,4-bis(oxyhexanoate) (C<sub>6</sub>PhC<sub>6</sub>Na<sub>2</sub>) system. The main reason for us to select carbonate bolas is their variable solution conditions with pH, which is expected to change the  $a$  value and then  $P$  of the self-assembled structures in these systems. In addition, inorganic salts, alkyl alcohol, and oppositely charged

\* Corresponding authors. E-mail: (J.H.) jbh Huang@pku.edu.cn and (Z.L.) zcli@pku.edu.cn.

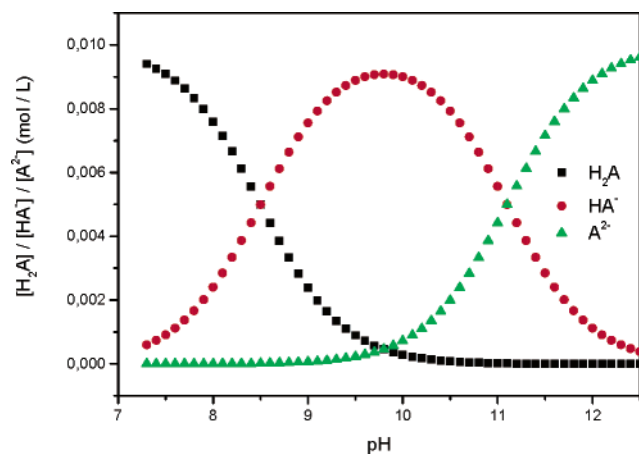
<sup>†</sup> College of Chemistry and Molecular Engineering.

<sup>‡</sup> College of Life Science.

**TABLE 1: Comparison of Geometrical Rule and Packing Parameter for Aggregates in Conventional Surfactant and Bolaamphiphile's Solution**

	conventional surfactant			symmetric bolaamphiphile		
	sphere	cylinder	bilayer	sphere	cylinder	monolayer
$V^a = gv_0$	$4\pi R^3/3$	$\pi R^2$	$2R$	$4\pi R^3/3$	$\pi R^2$	$2R$
$A$	$ga = 4\pi R^2$	$ga = 2\pi R$	$ga = 2$	$2ga = 4\pi R^2$	$2ga = 2\pi R$	$2ga = 2$
$a$	$3v_0/a$	$2v_0/R$	$v_0/R$	$3v_0/2a$	$v_0/R$	$v_0/2R$
$P = v_0/al_0$	$v_0/al_0 \leq 1/3$	$v_0/al_0 \leq 1/2$	$v_0/al_0 \leq 1$	$v_0/al_0 \leq 1/3$	$v_0/al_0 \leq 1/2$	$v_0/al_0 \leq 1$

<sup>a</sup>  $V$  and  $A$  are the volume and surface area of the aggregates, respectively, which refer to the entire spherical aggregate, unit length of a cylinder, or unit area of a bilayer.  $R$  is the radius of spherical or cylindrical micelle or the half-bilayer/monolayer thickness of the spherical vesicle.

**Figure 1.** Illustration of the relative contents of  $H_2A$ ,  $HA^-$ , and  $A^{2-}$  with pH in 10 mM  $C_6PhC_6Na_2$  solution ( $25 \pm 0.1$  °C).

conventional amphiphiles were also used to change the solution conditions. We did observe the morphology transformation between different bilayer structures with the addition of the previous additives, which indicates that the molecular packing parameter also works in the bolaamphiphile system.

## Materials and Methods

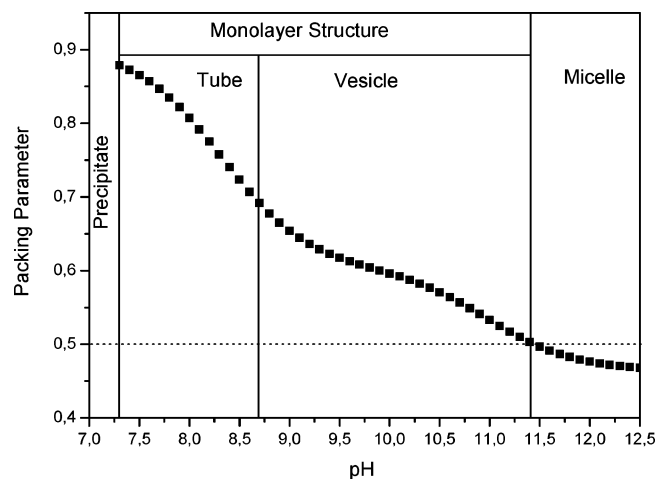
**Materials.** Bolaamphiphiles ( $C_6PhC_6Na_2$  and  $C_{10}PhC_{10}Na_2$ ) used in this study as illustrated in Scheme 1 were synthesized by our group.<sup>14</sup>

Dodecyltrimethylammonium bromide (DMAB), dodecyltriethylammonium bromide (DEAB), dodecyltripropylammonium bromide (DPAB), and dodecyltributylammonium bromide (DBAB) were prepared in the following ways: the equimolar mixture of 1-dodecyl bromide and trimethylamine, triethylamine, tripropylamine, or tributylamine, respectively, was refluxed for 30 h in ethanol. Then, the solvents were removed, and the solids were recrystallized 5 times in acetone/ether mixed solvents. The purity of all the surfactants was examined, and no minimum was found in the surface tension curve. Deionized water was treated with  $KMnO_4$  and distilled before use. Other reagents and solvents (AR grade) were from Beijing Chemical Co.

### Transmission Electron Microscopy (TEM) Measurements.

A uranyl acetate solution (1%) was used as a staining agent according to ref 25. One drop of the sample dispersion was placed onto a carbon Formvar-coated copper grid to permit the sample to be adsorbed on the grid (230 mesh), and the excess liquid was sucked away by using filter paper. Then, one drop of staining agent was placed onto the sample grid, and the excess liquid was sucked away again. The stained samples were examined in a JEOL-100CX (II) transmission electron microscope.

**Dynamic Light Scattering (DLS).** Dynamic light scattering measurements were carried out using a spectrometer of standard design (ALV-5000/E/WIN Multiple Tau Digital Correlator) with

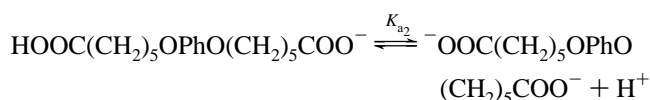
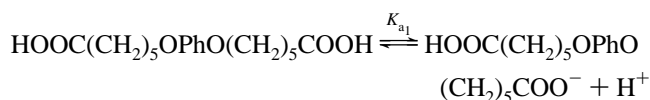
**Figure 2.** Packing parameter of 10 mM  $C_6PhC_6Na_2$  against pH. At a pH lower than 7.4,  $C_6PhC_6Na_2$  is water insoluble. The corresponding self-assemblies predicted by using packing parameters are also labeled in the graph. The shape of aggregate (tube and vesicle) is from the TEM result in the following text.

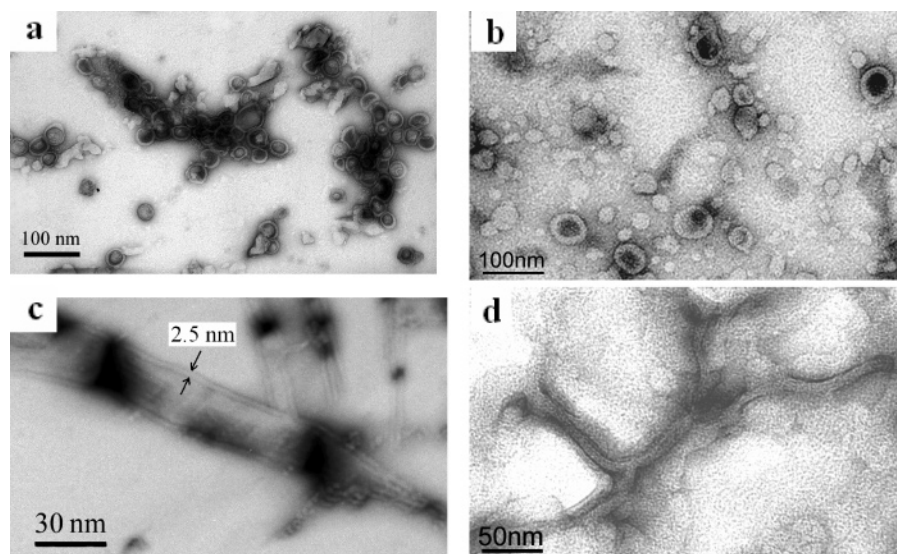
a Spectra-Physics 2017 200 mW He–Ne laser (514.5 nm wavelength). The scattering angle was  $90^\circ$ , and the intensity autocorrelation functions were analyzed using the methods of Cumulant and Contin. The apparent hydrodynamic radius ( $R_h$ ) was deduced from the diffusion coefficient  $D$  by using the Stokes–Einstein formula  $R_h = k_B T / (6\pi\eta D)$ . All measurements were made at  $25.0 \pm 0.1$  °C.

## Results and Discussion

**Molecular Packing Parameters in  $C_6PhC_6Na_2$  Aqueous Solution.** As mentioned in the Introduction, Nagarajan established the rules of molecular packing parameters for bolaamphiphiles,<sup>7</sup> which is the same in the final form as that for conventional surfactants. Table 1 shows the summation of the simple geometrical relations for spherical, cylindrical, or bilayer aggregates made up of bolaamphiphiles as well as those of conventional surfactant molecules. To test the previous predictions, we carried out the following experiments.

**Packing Parameter Varies with pH in the  $C_6PhC_6Na_2$  Aqueous Solution.**  $C_6PhC_6Na_2$  is soluble in water at  $pH \geq 7.4$ . In the aqueous solution of  $C_6PhC_6Na_2$ , the following equilibriums exist:





**Figure 3.** TEM images of aggregates formed in 10 mM  $C_6PhC_6Na_2$  aqueous solutions at different pH values. (a) pH 11.3; (b) pH 9.0; (c) pH 8.7; and (d) pH 7.4.

Therefore, three species (i.e.,  $HOOC(CH_2)_5OPHO(CH_2)_5COOH$  ( $H_2A$ ),  $HOOC(CH_2)_5OPHO(CH_2)_5COO^-$  ( $HA^-$ ), and  $^-OOC(CH_2)_5OPHO(CH_2)_5COO^-$  ( $A^{2-}$ )) coexist in the  $C_6PhC_6Na_2$  solution, but their relative concentrations will vary with pH. The concentrations of different components can be determined from  $pK_{a1}$  and  $pK_{a2}$  for a given  $C_6PhC_6Na_2$  concentration. By using the pH titration method, we obtained that  $pK_{a1} = 8.5$  and that  $pK_{a2} = 11.1$  at 25 °C, respectively. Therefore, the concentrations of the three components in the 10 mM  $C_6PhC_6Na_2$  solution varying with pH (Figure 1) were obtained by using the following three equations:

$$K_{a1} = \frac{[H^+][HA^-]}{[H_2A]} \quad (1)$$

$$K_{a2} = \frac{[H^+][A^{2-}]}{[HA^-]} \quad (2)$$

$$[A^{2-}] + [HA^-] + [H_2A] = 0.01 \quad (3)$$

It is clear from Figure 1 that, at  $7.4 \leq pH \leq 9.8$ , the concentration of  $A^{2-}$  is almost zero. The concentration of mono acid  $HA^-$  increases to a maximum, while the diacid  $[H_2A]$  decreases to a minimum with increasing pH. After pH 9.8, the concentration of  $HA^-$  begins to decrease, whereas  $[A^{2-}]$  begins to increase. At pH 12.5,  $[A^{2-}]$  reaches its maximum, but  $HA^-$  reaches its minimum. In this pH region ( $9.8 \leq pH \leq 12.5$ ),  $[H_2A]$  is almost zero. To simplify the situation with the discussion of packing parameters, we first consider the head group areas of  $H_2A$  and  $A^{2-}$ . It has been well-documented that the head group area of the long chain fatty acid is about  $20 \text{ \AA}^2$ ,<sup>26</sup> and that it increases to larger than  $39 \text{ \AA}^2$  if the acid group is fully dissociated.<sup>27</sup> To estimate the volume of the hydrophobic chain of  $C_6PhC_6Na_2$ , we assume the molecule to be a cylinder with a width of  $d_0$ . If we neglect the effect of the benzene ring on the molecular width,  $d_0$  can be approximately taken as the same as the normal fatty acid molecules of  $4.8 \text{ \AA}$ .<sup>28</sup> Therefore,  $v_0$  is expressed as  $l_0\pi(d_0/2)^2$ . Hence, the molecular packing parameter can be written as  $P = v_0/ao = l_0\pi(d_0/2)^2/ao = \pi(d_0/2)^2/a$ . For a system fully composed of  $H_2A$  or  $A^{2-}$ , the calculated  $P$  values are 0.90 or 0.46, respectively. These values indicate that the monolayer structure will be expected at low

**TABLE 2: Aggregate Morphologies in 10 mM  $C_6PhC_6Na_2$  Solution at Different pH Values**

pH aggregates	$7.4 \leq pH \leq 8.7$	$8.7 < pH \leq 11.5$	$pH > 11.5$
	Tubes	vesicles	micelles

pH values, whereas micelles will be expected at high pH values in the  $C_6PhC_6Na_2$  system.

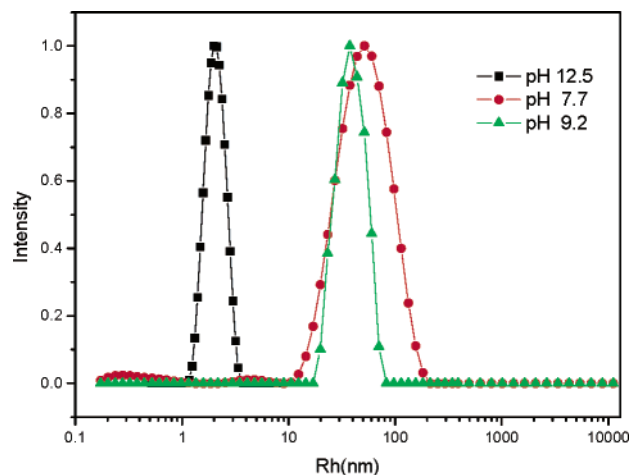
We can also roughly estimate the head group area of  $HA^-$  to be approximately  $33 \text{ \AA}^2$  by simply averaging the areas of  $H_2A$  and  $A^{2-}$ . (For the mixed systems containing ionic molecules, the relations between composition and areas are actually nonlinear. Here, we only make some rude calculations.) In this way,  $P$  at different pH values was calculated and plotted in Figure 2.

According to this graph, one can expect a monolayer structure at  $7.4 \leq pH \leq 11.4$  and rod-like micelles at pH values higher than 11.5 in the 10 mM  $C_6PhC_6Na_2$  solution. Considering that the head group area  $39 \text{ \AA}^2$  of the dissociated acid group is obtained with surface pressure methods, which leads to rather dense packing of the head groups, the actual area must be larger than  $39 \text{ \AA}^2$ . Actually, the surface areas of decyl and dodecyl carbonate acid at pH 13 in a  $0.13 \text{ mol kg}^{-1}$  solution are both  $45 \text{ \AA}^2$ .<sup>29</sup> Therefore, the error of the packing parameter calculated in this way in a high pH range is rather large, and the  $P$  value must be smaller than 0.46, so rod-like micelles probably do not exist at all. This estimation is proven by the experimental results in the following text.

**Aggregate Morphology in  $C_6PhC_6Na_2$  Solution at Different pH Values.** To test the previous predictions, we observed the aggregation behavior of  $C_6PhC_6Na_2$  at different pH values by using TEM. At pH values higher than 11.5, no aggregates were observed, which is probably due to the size of the micelles being too small for the resolution of TEM. However, vesicles with diameters of about 20 to  $\sim 80 \text{ nm}$  in  $8.7 < pH \leq 11.5$  (Figure 3a,b) and tubes that were 10 nm wide and 100 to  $\sim 200 \text{ nm}$  long in the  $7.4 \leq pH \leq 8.7$  solution were seen (Figure 3c,d). The TEM observation results are also shown in Table 2.

The previous solutions were also measured with dynamic light scattering. For the pH 12.5 solution, only a peak at  $R_h \approx 2 \text{ nm}$  was seen, which is probably from micelles in the system. In contrast, both Cumulant and Contin methods revealed particles of  $R_h \approx 37.8$  and  $51.2 \text{ nm}$  for the pH 9.2 and pH 7.7 solutions, respectively (Figure 4). Moreover, the polydispersity in the pH 9.2 solution is smaller than that in the pH 7.7 solution. This





**Figure 4.** pH effect on the hydrodynamic radius distribution in the  $C_6PhC_6Na_2$  aqueous solution. Measurements were carried at  $25 \pm 0.1$  °C.

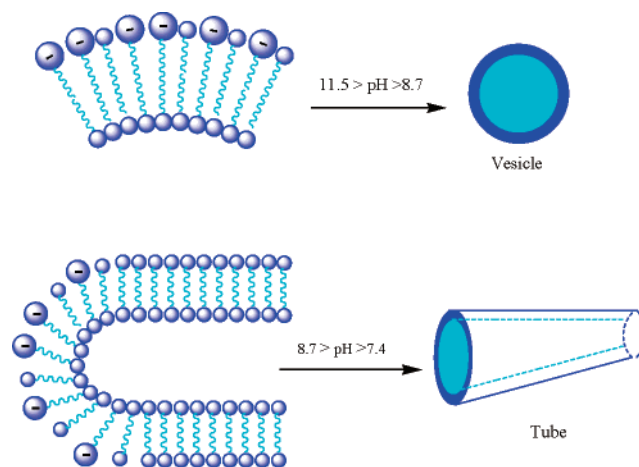
result is in good agreement with the TEM observations because tubes have more conformations than what vesicles have in the solution. It is clearly revealed in Figure 3c that the thickness of the tube membrane is about 2.5 nm, which is quite close to the extended molecular length of  $C_6PhC_6Na_2$  from the Chem 3-D model (2.2 nm). In addition, the membrane thickness for both the vesicles and tubes from the XRD<sup>30–32</sup> method is 2.15 nm (see Supporting Information). Therefore, we can conclude that the monolayered membrane has been formed in these solutions, which agrees well with the prediction of the molecular packing parameters.

It is also interesting to note that it seems that the  $P$  value for tubes is larger than that for vesicles in the  $C_6PhC_6Na_2$  solution. We found tubes in  $0.7 \leq P \leq 1$  but vesicles in the  $0.5 \leq P < 0.7$  region. Of course, this category for the tubular and vesicular  $P$  range is rather rough, and the conclusion has to be tested by more experimental data. At least, the present finding is reasonable with respect to the curvature of the aggregates. At  $7.4 \leq pH \leq 8.7$ , the bola molecules in the form of  $HA^-$  are less than 60%, and most of them are  $H_2A$  (i.e., less than 30% head groups are charged in this region). Therefore, the charge density on the surface of the self-assemblies is quite low, which is in favor of the formation of monolayer structures with low curvature tubes in this study. As to the pH range of 8.7 to  $\sim 11.5$ , we can discuss two situations: (1)  $8.7 \leq pH \leq 9.8$ . In this stage, the percentage of  $HA^-$  continues to increase and reaches a maximum of nearly 100%. (2) At  $9.8 \leq pH \leq 11.5$ , the percentage of  $HA^-$  decreases but that of  $A^{2-}$  begins to increase. In both cases, the charge density increases until 65% of the head groups is charged at pH 11.5. Therefore, the curvature of the self-assembly will increase due to the repulsive interaction between the head groups—this could be the reason for the formation of vesicles. The formation of tubes and vesicles in the  $C_6PhC_6Na_2$  solutions is illustrated in Scheme 2.

**Aggregate Morphology Manipulation with Additives.** The previous experiments suggest that the molecular packing parameter also works in the bolaamphiphile system. Therefore, we can manipulate the aggregate morphology transformation by modifying the solution conditions.

**Influence of NaBr and Octanol on the Aggregates.** As described in the previous sections, only micelles with relatively small  $P$  values exist in the pH 12.5  $C_6PhC_6Na_2$  solution. Now, we tried to increase the  $P$  value by the addition of octanol or NaBr to this solution. The addition of NaBr will reduce the repulsion between the head groups due to the screening of

**SCHEME 2: Aggregate Formation at Different pH Values in 10 mM  $C_6PhC_6Na_2$  Solutions**



charges on them. This shielding of charge will of course decrease the  $a$  value, so as to increase  $P$ . The addition of octanol will not only reduce the repulsion between the head groups but also increase the volume of the hydrophobic tail. Therefore, a decrease in  $a$  but an increase in  $v_0$  will be expected. Both factors tend to enhance the  $P$  value. As expected, we did observe vesicles after the addition of 50 mM NaBr or 0.3 mM octanol to the pH 12.5  $C_6PhC_6Na_2$  solution (Figure 5a,b). The enlarged vesicles clearly displayed that the thickness of the membrane is also 2.5 nm, which indicates the similarity of the membrane to that of the tubes in the pH 8.7 solution.

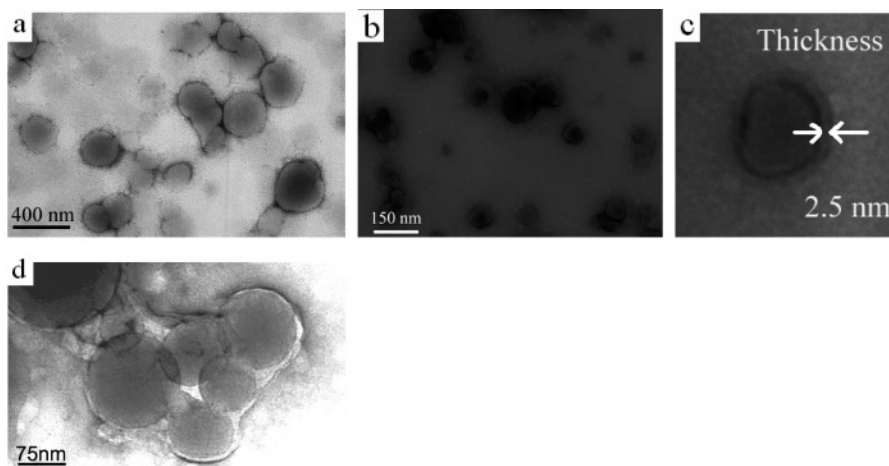
**Influence of Solvent Property on the Aggregate Morphology.** Next, we studied the effect of small alcohols, such as ethanol, on the aggregate morphology. The addition of ethanol to the system lowers the polarity and the dielectric constant of the solvent.

$$F = \frac{q_1 q_2}{4\pi\epsilon r^2} \quad (4)$$

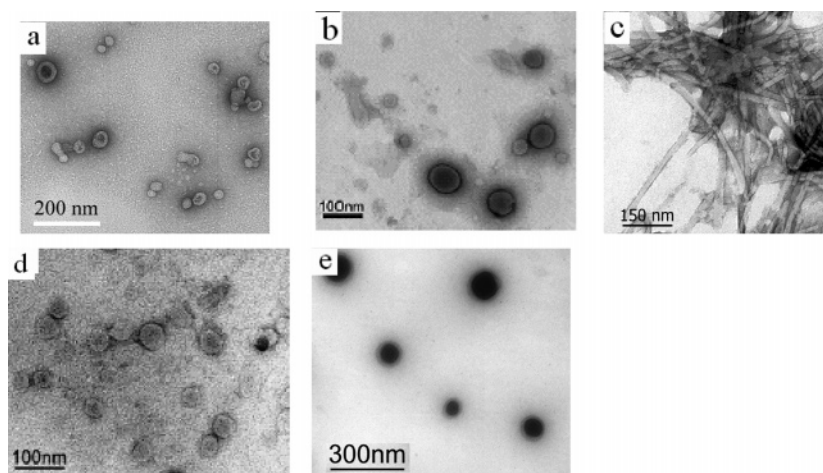
According to eq 4, we know that the repulsive interaction ( $F$ ) between two charged head groups will increase with lowering the dielectric constant ( $\epsilon$ ) of the media, as is equal to increase  $a$ . Therefore,  $P$  will be lowered. Interestingly, after the addition of 5% (v/v) ethanol to the pH 7.7 solution, tubes were found to transform into vesicles (Figure 5d). This observation also coincides with our theoretical calculation of  $P$  for tubes being larger than that of vesicles.

**Head Group Effect on the Aggregate Morphology in the  $C_nPhC_nNa_2$ /Cationic Conventional Surfactant Mixed Systems.** It is well-known that vesicles can be formed in the mixed systems of conventional cationic/ionic surfactants<sup>33</sup> and oppositely charged bolaamphiphile/conventional surfactants.<sup>15–19</sup> Similarly, vesicles were also observed in a series of mixtures of  $C_6PhC_6Na_2$ /conventional cationic surfactants.

Four conventional surfactants with the same hydrophobic chain but with different sizes of the head groups (i.e., dodecyltrimethylammonium bromide (DMAB), dodecyltriethylammonium bromide (DEAB), dodecyltripropylammonium bromide (DPAB), and dodecyltributylammonium bromide (DBAB)) were used to form mixed systems with bolas. As the head groups increased in the order of trimethyl, triethyl, tripropyl, to tributyl, only vesicles were found in all the mixed systems (Figure 6a,b). This is probably because of the two aspects of factors that determine the  $a$  value. Besides the size of the surfactant head group itself, the interactions between the head groups, especially



**Figure 5.** TEM images in 10 mM  $C_6PhC_6Na_2$ . (a) pH 12.5, 50 mM NaBr; (b) pH 12.5, 0.3 mM  $n-C_8OH$ ; (c) magnification (from panel b) of the vesicles giving a membrane thickness of about 2.5 nm, which is nearly the same length as the  $C_6PhC_6Na_2$  molecule; and (d) pH 7.7,  $V(H_2O)/V(ethanol) = 1:0.05$ .



**Figure 6.** Vesicles formed in the mixed systems. (a) 1:2  $C_6PhC_6Na_2/DMAB$ ; (b) 1:2  $C_6PhC_6Na_2/DPAB$ ; (c) 1:4  $C_{11}PhC_{11}Na_2/DEAB$ ; (d) 1:4  $C_{11}PhC_{11}Na_2/DPAB$ ; and (e) 1:4  $C_{11}PhC_{11}Na_2/DBAB$ . All the experiments were carried out at pH 9.2.

in the ionic surfactant systems, also play an important role. In the mixed systems of anionic bola surfactant and cationic surfactant, the electrostatic interaction is very strong at the mixing ratio of 1:2, which greatly reduced the contribution of the size variation of the cationic surfactant head groups to the  $a$  value. Therefore, the overall  $P$  values influenced by the change of the cationic surfactant head groups were so small that no transformation of organized assemblies was observed. On the basis of this viewpoint, the head group effect will be more obvious if we increase the hydrocarbon chain of bolaamphiphile in the mixed systems since larger values of  $v_0/l_0$  help to enlarge the final  $P$  value. Actually, we did observe the aggregate transformation in the series of the  $C_{11}PhC_{11}Na_2/DE$  (P, B) AB mixed system. It is clear in Figure 6c that tubes were found in the  $C_{11}PhC_{11}Na_2/DEAB$  system, while vesicles were found in the  $C_{11}PhC_{11}Na_2/DPAB$  and  $C_{11}PhC_{11}Na_2/DBAB$  mixed systems (Figure 6d,e). It should be noticed that in the previous mixed systems, the mixing ratio between bolas and surfactants was not 1:2 but 1:4 because  $C_{11}PhC_{11}Na_2$  is water insoluble under all pH values but can form homogeneously mixed solutions with DEAB, DPAB, and DBAB at mixing ratios higher than 1:3. This changing of the mixing ratio apart from 1:2 can reduce the contribution of the electrostatic attraction to the  $a$  value, which also makes the head group effect more obvious. Therefore, the transformation from tubes to vesicles was successfully realized by the variation of cationic surfactant head

groups, which confirmed that the molecular packing theory was also effective in the mixed systems of bolas and conventional oppositely charged surfactants.

### Conclusion

Molecular packing parameters were generalized to symmetric bola systems. The experimental results in the  $C_6PhC_6Na_2$  systems indicate that the aggregate morphology of bolas can also be predicted as that of conventional surfactants. By increasing the pH,  $P$  was decreased due to the increase of the head group area, and tubes were transformed into vesicles and vesicles to micelles. By adding NaBr and octanol to the systems,  $P$  was increased due to the decrease of  $a$ , and vesicles were transformed into tubes and micelles into vesicles. The molecular packing theory was also effective in the mixed systems of bolas and conventional oppositely charged surfactants. In the mixed systems with long hydrocarbon chain bolaamphiphiles at unelectroneutral mixing ratios,  $P$  decreases with increasing the head group size of surfactant, which results in the transformation from tubes to vesicles.

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