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Spontaneous Vesicle Formation in Mixed Aqueous Solution of Poly-tailed Cationic and Anionic Surfactants

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Abstract: Spontaneous vesicles from the mixed aqueous solution of poly-tailed cationic surfactant PTA and anionic surfactant AOT are firstly obtained. Vesicle formation and characterizations are demonstrated by negative-staining TEM and dynamic light scattering. A monodisperse vesicle system is obtained with a polydispersity of 0.082. Ultrasonication can promote the vesicle formation. Mechanism of vesicle formation is discussed from the viewpoint of molecular interaction.

Keywords: Vesicle, dynamic light scattering, negative-staining TEM, spontaneous formation.

Vesicles are the closed bilayer membranes made up of surfactants, whose structure is very similar to the cell membranes. To date, spontaneous vesicles formed from single DDAOH[1], oppositely charged surfactants[2], two different cationic surfactants[3], anionic and zwitterionic surfactants[4] have been reported. These spontaneous vesicles are believed to be thermodynamically stable, and their size, charge and permeability can be readily adjusted by varying the relative amounts and /or chain lengths of the two surfactants.

A new vesicle system of the aqueous mixture of PTA and AOT has been obtained in our lab. The characterizations are demonstrated by negative-staining TEM and the dynamic light scattering experiments.

Experimental

Tri-(dodecyl-dimethyl-hydroxypropyl ammonium chloride) phosphate (PTA, $O{=}P[OCH_2CH(OH)CH_2N^+(CH_3)_2C_{12}H_{25}]_3 \cdot 3Cl^-$) donated by Research Institution of Jinling Petrochemical Corporation was doubly purified; sodium bis-(2-ethylhexyl) sulfosuccinate (AOT) was obtained from Fluka Co. without any further purification;

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NaCl from Shanghai Chemical Co. was A.R. grade; water was double-distilled.

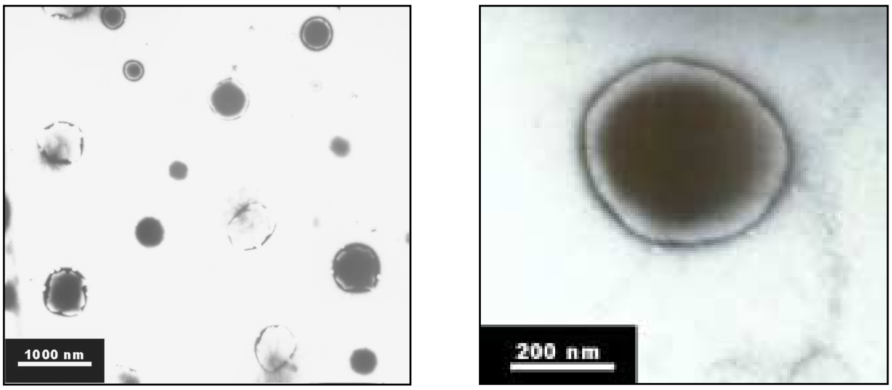
Observation of Vesicles by JEM-1200EX transmission electron microscope (TEM, JEOL Ltd., Japan) was performed with a negative-staining method. The diameter of vesicle was determined by the dynamic light scattering method (DLS, Brookhaven Instrument Co., Model BI-300SM) with an argon ion laser operating at 488 nm. All measurements of DLS were made at the scattering angle of 90° at a temperature of 25℃.

Results and Discussion

Self-formation of PTA-AOT vesicle

PTA and AOT aqueous solutions, which are both of 1.0×10^{-3} mol • L^{-1}, are mixed at the volume ratio from 1:9 to 9:1 at 25°C. Transparent or turbid blue solutions were obtained, which indicated the formation of vesicle[3]. When the total surfactant concentration increased, the blue color of the mixing system got deeper. The negative-staining TEM photographs affirmably proved the existence of vesicles.

Figure 1 Negative-staining TEM photograph (PTA/AOT=1/9, C_{total} =2.0×10^{-2} mol/L)



Study on the diameter and polydispersity of vesicles

The size and polydispersity of vesicle was measured by dynamic light scattering method (**Table 1**). The diameter of aggregation firstly increased with the increase of PTA ratio and then decreased. The diameter was in the range of 100 ~ 240 nm and the polydispersity is almost below 0.30, which indicated the narrow size distribution. The polydispersity at the mixing ratio of 1/9 (PTA/AOT) is only 0.082 and a sharp peak appears in the spectrum (**Figure 2**). Two or more distribution peaks appearing in most spectrums showed a much wider size distribution.

The vesicle diameter changed with the mixed ratio. When the mixed ratio was 9/1(PTA/AOT), only a few of AOT molecules penetrated into a large number of PTA molecules. The ion-complexes with a big curvature formed vesicle of small diameter. With the penetration of more AOT molecules, the curvature got smaller and the formed vesicle became larger and larger, and the largest vesicles were obtained in the mixed ratio of 3/7 (PTA/AOT). Furthermore AOT molecules would produce the unstable bilayer and the recombination occurred resulting in the ion-complex with bigger curvature, and diameter of vesicles thus obtained become smaller.

Table 1 The diameter and polydispersity of the vesicles

PTA / AOT	1/9	2/8	3/7	5/5	6/4	7/3	8/2	9/1
D (nm)	147.0	176.7	237.8	208.0	160.1	124.8	114.6	102.6
Polydispersity	0.082	0.133	0.267	0.24	0.144	0.238	0.224	0.241

Note: C_{total} =1.0×10^{-3} mol/L

The increasing of total surfactant concentration can promote the growth of vesicle resulting in the increase of diameter (**Figure 3**). We can see that vesicle diameter at various mole ratio increases dramatically at higher total surfactant concentration. Especially in the PTA-rich system the concentration has a greater effect on the vesicle diameter than that in the AOT-rich system.

Figure 2 Spectrum for size distribution of vesicle (PTA/AOT=1/9)

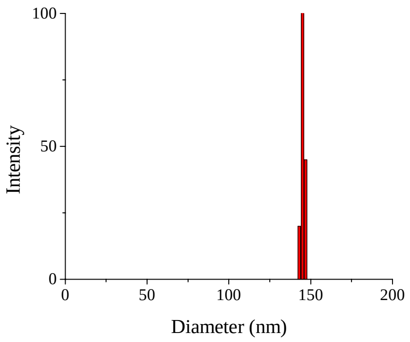
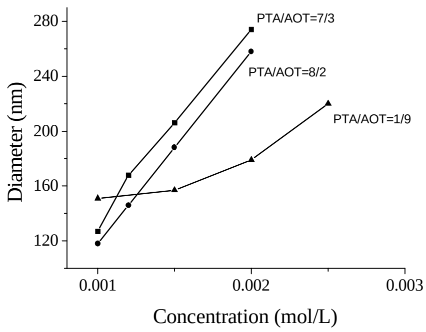


Figure 3 Vesicle diameter varies with the total surfactant concentration



The effect of ultrasonication

After ultrasonication for 30 mins, the blue of the solution was deeper and the turbidity increased, which indicated that ultrasonication had effect on formation of vesicle. The diameters of vesicles decreased after ultrasonication (**Table 2**). It could be explained that the ultrasonication performed mechanical force to the molecules, which made vesicle diameter decrease.

Table 2 The effect of ultrasonic on diameter and polydispersity of the vesicles

PTA / AOT (C_{total} =1.0×10^{-3} mol/L)	1/9	2/8	3/7	5/5	6/4	7/3	8/2
D (nm)	147.0	176.7	237.8	208.0	160.1	124.8	114.6
Polydispersity	0.082	0.133	0.267	0.24	0.144	0.238	0.224
D (nm)	128.6	155.8	194.2	173.8	137.2	117.3	95.4
Polydispersity	0.110	0.140	0.221	0.246	0.158	0.153	0.199

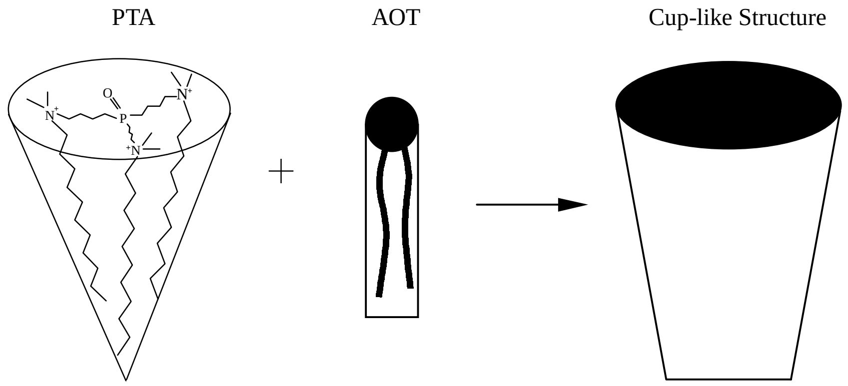
Note: Data in upper row without ultrasonication; under row ultrasonication for 30 mins.

Mechanism of spontaneous vesicle formation

The geometries of surfactants are important factors dominating the geometries of aggregates. AOT molecule is cylindric because of the preponderant *trans* and *gauche* conformations[5, 6]. PTA is triammonium phosphate with three hydrophobic carbochains, which converge closely into conoid directing the apolar region. Three N atoms of quaternary ammonium with positive charge are connected with the ester-bonds of phosphate through the hydroxypropyl, forming a giant polar head. So the geometry of PTA molecule is conical or cup-like (**Figure 4**).

The cup-like structure is formed because of the electrostatic attraction between PTA and AOT (**Figure 4**), which is easily to form vesicle according to the Masaniko[7]. The blue is deeper with the increase of total surfactant concentration, which leads to the increase of the amount and diameter of vesicles.

Figure 4 Geometric structure of surfactants and the ion-complex



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