

Spontaneous vesicle formation in aqueous solution of zwitterionic and anionic surfactant mixture

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Abstract

Vesicles form spontaneously in the aqueous mixtures of dodecyl sulfonate betaine (DSB) and sodium bis(2-ethylhexyl) sulfosuccinate (Aerosol OT (AOT)) at certain mixing ratios, which has been demonstrated by microcalorimeter, negative-staining transmission electronic microscopy (TEM) and quasi-elastic light scattering (QELS) methods. The addition of NaCl will expand the range of vesicle formation, and monodispersed vesicles are obtained in the solution from the salinity of 0.03 to 0.09 M at the mixing molar ratio of 7/3 (DSB/AOT, mol/mol), with the polydispersity of the system lower than 0.1. To learn more about the structural change in the mixture, ultrasonic was employed finally. Meanwhile analysis was made from the viewpoint of molecular geometry structure. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Vesicles are substantially valuable in biomimicking [1], drug delivering [2], synthesis of nanoparticles [3] and microreactors [4]. Two kinds of methods are involved in the vesicle formation. The formation from phospholipid usually requires input of some form of energy, for example, ultrasonic [5]. The vesicles thus formed are believed to be metastable and easy to fuse. On the other

hand, spontaneous vesicles prepared from aqueous mixtures of widely available surfactants of simple structures have attracted a great interest in the last few years, for example, from DDAOH [6], oppositely charged surfactants [7,8], and even two cationic surfactants[9]. These spontaneous vesicles are believed to be thermodynamically stable, and their size, charge, or permeability can be readily adjusted by varying the relative amounts and/or chain lengths of the two surfactants.

In this paper, we report a spontaneous vesicle formation from a zwitterionic surfactant, dodecyl sulfonate betaine (DSB) and an anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) at

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certain mixing ratios in aqueous solution. The addition of salt expands the range of vesicle formation, which has been demonstrated by microcalorimeter, negative-staining transmission electronic microscopy (TEM) and quasi-elastic light scattering methods (QELS). More important, monodispersed vesicles are obtained by controlling the salinity, with the polydispersity lower than 0.1 at the mixing molar ratio of 7/3 (DSB/AOT, mol/mol, total surfactant concentration of 1 wt.%). Finally the diameter of the vesicles is compared with those obtained after being ultrasonicated, so that the structural change of the aggregate and the mechanism of vesicle formation can be got from the viewpoint of geometry.

2. Experimental section

2.1. Materials and preparation of vesicles

Dodecyl sulfonate betaine (DSB) was donated by Nanjing Chemical Co. which was A.R. grade without any further purification; sodium bis(2-ethylhexyl) sulfosuccinate (AOT) was doubly purified, NaCl from Shanghai Chemical Co. was A.R. grade, water was doubly distilled. Samples were prepared by first mixing stock solutions of both zwitterionic and anionic surfactant at desired concentration in distilled water. Stock solutions were equilibrated at room temperature and filtered through a 0.2 μm filter prior to preparing samples. Vesicles were prepared by mixing stock solutions at the desired molar ratio, NaCl was added after being accurately weighed. After brief vortex mixing, the solutions were not subject to any type of mechanical agitation. All samples were equilibrated at 25°C in a thermostated bath for a month.

2.2. Microcalorimeter

The determination of thermal change in the formation was made by using a 2277 type thermal activity monitor, made by LKB in Sweden. NaCl was dissolved in advance and thermostated together with the other samples for 3 h at 25°C, and then added into the mixture at the mixing ratio of

7/3 and 3/7 (DSB/AOT), respectively, after the baseline ran horizontally. Then the thermal change during the mixing was recorded instantly. The heat of dilution could be omitted.

2.3. Observation of the vesicles

The vesicles were observed with a TEM by using the negative-staining method. As soon as the surfactant mixture solution and an aqueous solution of 2% phosphotungstic acid (PTA, pH 7) were mixed volumetrically at the ratio of 2:1, the resultant solution was then added dropwise to a 150-mesh copper grid coated with colloidal, sprayed with a carbon film. Extra droplet was instantly removed by using a filter paper, and then the grid was dried in a vacuum desiccator for 6 h as a TEM sample.

2.4. Determination of the diameter and polydispersity of vesicles

The diameter of vesicles was determined by using the QELS, which was made with a spectrometer of standard design (Brookhaven Model BI-300SM goniometer and Model BI-9000AT correlator) and a 300 mW Ar laser. All measurement was made at the scattering angle of 90° at 25°C, and the intensity of function was analyzed by the method of cumulants.

3. Results and discussion

Compared with the single component surfactant system, the mixed surfactant system can produce more kinds of aggregates by adjusting composition and interaction.

3.1. Mixture of DSB and AOT

The solution containing 0.5 wt.% DSB was mixed with that of 0.65 wt.% AOT at the following ratio to keep the molar ratio at 1:1 at equal volume. The visible change of the appearance in turbidity is given in Table 1.

The appearance of the mixture of the zwitterionic and anionic surfactant was different from

Table 1
Visible change of appearance after mixing the two solutions of DSB and AOT

DSB:AOT (mol:mol)	1:9	2:8	3:7	4:6	5:5	6:4	7:3	8:2	9:1
Appearance	Bluish turbid	Bluish turbid	Bluish turbid	Bluish turbid	Bluish turbid	Bluish turbid	Clear	Clear	Clear

that of cationic and anionic surfactant. At the first sight, they are transparent and colorless after mixing. But after a while, bluish turbidity appears gradually in the solution at the mixing ratio from 1/9 to 6/4, which designates the existence of vesicles [10]. The most turbid one is at the ratio of 5:5. The mixture keeps clear at the ratio from 7/3 to 9/1 at any time.

3.2. Effect of NaCl on the mixture of DSB/AOT

Primarily, we try to change the pH to improve the interaction between them to get a larger extent of vesicle formation. But further experiments prove that the salinity has a more significant effect. A slight addition of NaCl promotes the formation of vesicles evidently, which can be demonstrated by the thickening of turbidity and the bluish of the solution. At the mixing ratio of 7/3, the original clear and colorless solutions turn bluish and turbid abruptly after the addition of salt. But at the ratio of 8/2 and 9/1, there is no bluish all along no matter how much salt is added. In the following studies, the effect of NaCl on the formation of vesicles was expressed by microcalorimeter, TEM, QELS methods, especially at the ratio of 7/3 (DSB/AOT).

The microcalorimeter experiment gives an evidence of the formation of large aggregates. Fig. 1 depicts a sharp increase of heat after the addition

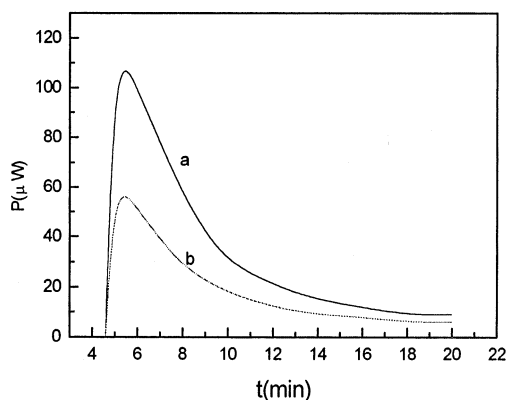


Fig. 1. Thermal activity monitored after the addition of NaCl of 0.03 M. Total surfactant concentration 1 wt.%. (a) Mixing ratio of 7/3 (DSB/AOT); (b) mixing ratio of 3/7 (DSB/AOT).

of NaCl in the mixture of 7/3 and 3/7 (DSB/AOT), which is an endothermic process. It reveals that there must be large aggregates formed. The endothermic peak of the mixture 7/3 is twice higher than that of 3/7, which can be attributed to the already existing vesicles in the latter mixture, so less heat to form vesicles is needed.

Fig. 2 gives the images of the vesicles in the 2 wt.% mixture at the mixing ratio of 7/3 at salt concentration of 0.09 M. Fig. 2(a) and (b) are single vesicles, the diameter of which is about 200 nm; Fig. 2(c) is combined vesicles which looks like a peanut and one can tell bilayer from the thin edge of the vesicle. Its apparent diameter is about 300–400 nm, which may contribute to the explanation for the polydispersity measured by QELS, as demonstrated later. Fig. 2(d) shows several structures like parachutes, they should be some disintegrating vesicles during the preparation.

From the data of dynamic light scattering, one can obtain not only the size of the particles, but also the size distribution expressed by polydispersity. For example, the micellar system is taken as monodispersed, which has a polydispersity less than 0.1 [11]. Originally, there exist various aggregate structures in the mixture without salt, including mixed globular micelles, mixed rod-like micelles, combined vesicles, etc. So there exist many peaks in the spectrum. The polydispersity of such a solution is usually higher than 0.2 (see Table 2). The addition of salt promotes the formation of vesicles, but does not improve the polydispersity of the system, except at the ratio of 7/3. There are always two or more distribution peaks in the spectrum, as shown in Fig. 4(b). In the mixing ratio of 8/2 and 9/1, there are no large vesicles formed all along.

In the solution of the mixing ratio of 7/3 (DSB/AOT), vesicles form quickly and the diameter increases markedly after adding NaCl, which reaches the maximum 118 nm at about 0.03 M of NaCl concentration, as shown in Fig. 3. The most attractive is the variety of the polydispersity of the system; it decreases continuously with the increase of salinity, and keeps lower than 0.1 from 0.03 to 0.09M, and even reaches 0.06 at 0.03 M NaCl, which can be regarded as a typical monodispersed system (see Fig. 4(a)).

Table 2
The diameter and polydispersity of the vesicles in the mixture at different NaCl concentration^a

DSB/AOT	C_{NaCl} (M) 0		0.03		0.06		0.09		0.12	
	D (nm)	Poly-dispersity	D (nm)	Poly-dispersity	D (nm)	Poly-dispersity	D (nm)	Poly-dispersity	D (nm)	Poly-dispersity
1:9	22	0.560	36	0.350	46	0.280	49	0.333	44	0.274
2:8	34	0.28	58	0.276	43	0.280	46	0.26	55	0.27
3:7	39	0.226	65	0.235	72	0.274	74	0.234	58	0.235
4:6	52	0.191	62	0.263	70	0.274	31	0.243	58	0.211
5:5	86	0.192	77	0.248	56	0.312	44	0.59	2.5	0.52
6:4	70	0.206	60	0.205	70	0.255	55	0.249	17	0.236
7:3	1.9	0.355	116	0.06	110	0.09	87	0.105	35.8	0.27
8:2	2.1	0.407	24.3	0.287						
9:1	1.8	0.55								

^a Total surfactant concentration 1 wt.%.

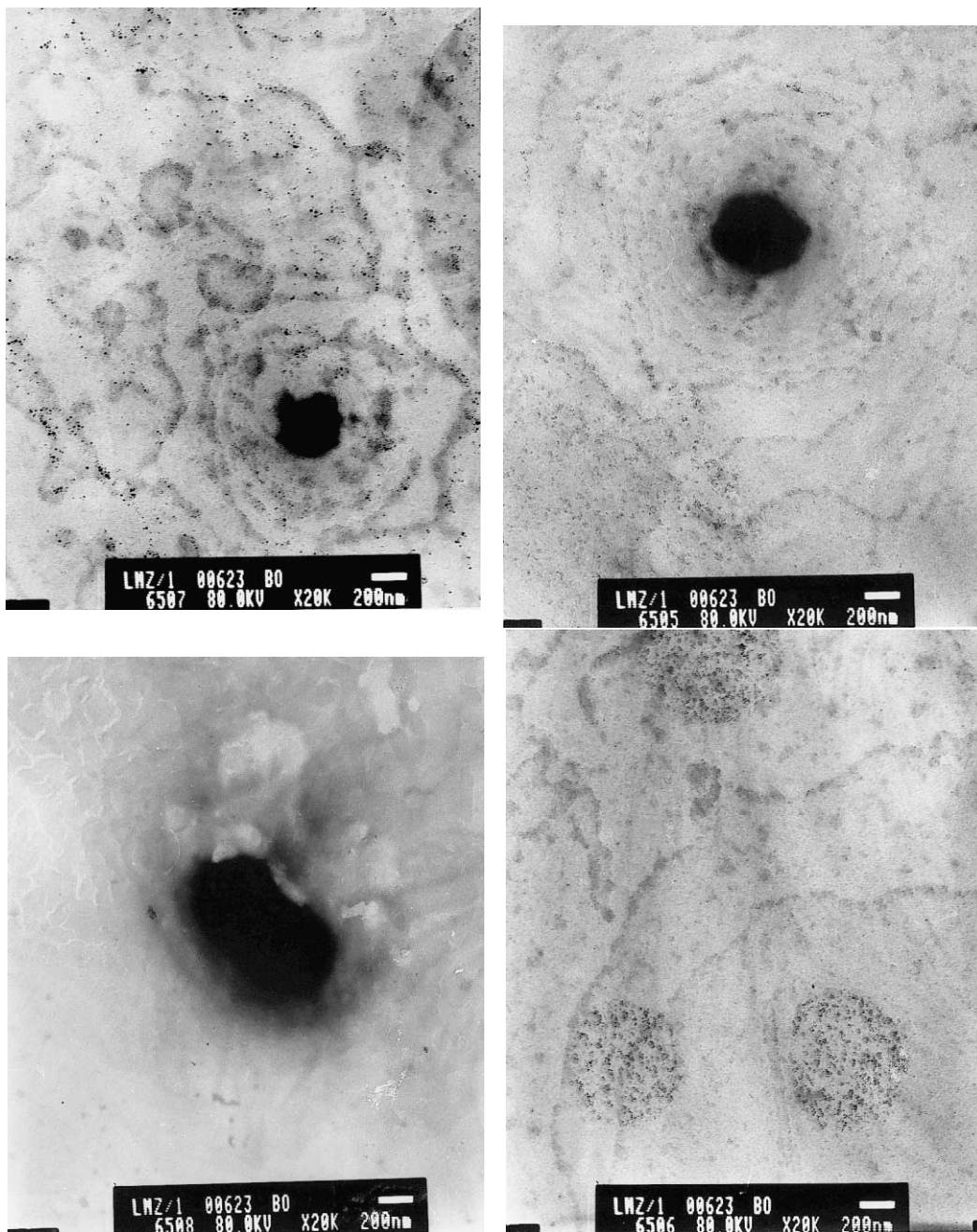


Fig. 2. TEM photographs of vesicles obtained by negative-staining method. $C_{SAA} = 2\%$, $C_{NaCl} = 0.09$ M, DSB/AOT = 7/3.

3.3. Effect of surfactant concentration on the vesicles formation

Vesicles grow with the increase of the concen-

tration of the surfactants. But the polydispersity of the system increases simultaneously due to the combination of vesicles even for the mixture at the ratio of 7/3 DSB/AOT. Fig. 5 shows the

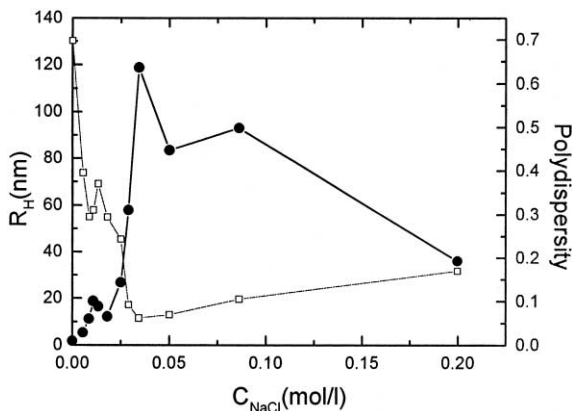


Fig. 3. Variation of diameter and polydispersity of the vesicles with the increase of NaCl concentration. ●, R_H ; □, polydispersity; $C_{SAA} = 1\%$; DSB/AOT = 7/3.

diameter of vesicles in the solution of the mixing ratio of 7/3 (DSB/AOT), at concentration of 2 wt.%, 0.09 M NaCl, is about 200 nm, which is in full agreement with that imaged with TEM.

3.4. Effect of ultrasonic on the further aggregation of vesicles

It is found that there always exists a distribution peak greater than 200 nm in the light scattering spectrum even in a clear mixture (see Fig. 4(b)). It is not in accordance with its appearance, which should be turbid if containing them. It is estimated as rod-like micellae. To determine its structure, ultrasonic was applied to such mixtures.

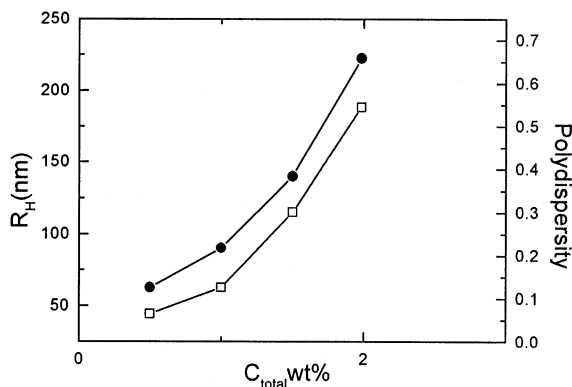


Fig. 5. Variation of the diameter of vesicles with the increase of surfactant concentration. ●, R_H ; □, polydispersity; DSB/AOT = 7/3; $C_{NaCl} = 0.09$ M.

During the preparation of vesicles, ultrasonic was a general method to donate surfactant molecules energy, and make them gather into a bilayer, bend and close to form vesicles. In the mixture of DSB and AOT, we obtain quite different results for differently dispersed systems after being ultrasonicated. For a monodispersed system, it is still monodispersed after ultrasonicated 30 min while the diameter of the vesicle increases evidently from 110 to 180 nm, which indicates the vesicles combine and fuse into large vesicles after gaining energy. But for a polydispersed system, which usually has two distribution peaks in the spectrum, there are two different results. If the system is AOT-rich, the final spectrum still has

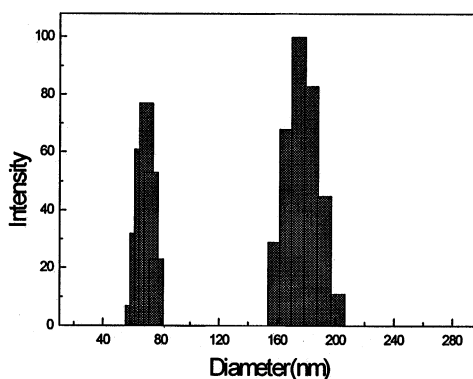
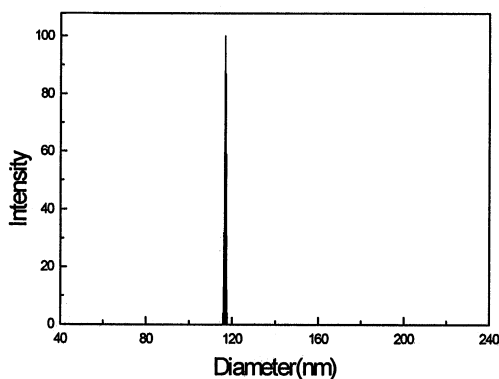


Fig. 4. Spectrum of quasielastic light scattering (QELS) of the mixture of DSB/AOT ($C_{SAA} = 1\%$, $C_{NaCl} = 0.03$ M). (a) DSB/AOT = 7/3 (w/w%); (b) DSB/AOT = 3/7 (w/w%).

two distribution peaks (Fig. 4(b)), but for a DSB-rich mixture, the system becomes monodispersed after being ultrasonicated, the diameter of vesicles increases a lot. It reveals that to form monodispersed vesicles, a proper ratio of the surfactants is necessary.

3.5. Mechanism of the formation of vesicles

In terms of geometry, there are two methyl around the atom N in DSB molecule, and the molecule has a long tail which make itself look like a conic, whereas the molecule of AOT has two tails and looks like a cylinder. The combination of them will form a cuplike structure (Fig. 6). According to the model of Masaniko [11], the conic structure is liable to form micellae and that of cylinder is liable to form bilayers, the cup-like structure will form vesicles. After the mixing of DSB and AOT, they will form mixed micellae due to the electric attraction and lay a foundation of a cuplike structure. But the electric attraction between DSB and AOT is actually weak, because the molecule of DSB is not evidently positive. In addition, the thick electric bilayer will also weaken the attraction, so the vesicle can form only at certain mixing ratios in the system, i.e. from 1/9 to 6/4 (DSB/AOT) when AOT is enough for the formation of a cuplike structure. The addition of salt promotes the formation, it compresses the electric bilayer of both molecules and gradually makes them approach to form a cup-like structure and then form vesicles.

With the increase of salinity, the two polar headgroups of the two surfactant molecules approach nearer. The area of the upper bottom of

the cuplike structure becomes smaller, more and more molecules enter the bilayer of the vesicle, which leads to the decrease of the curvature and the increase of the diameter. But on the other hand, the more the bilayer is compressed, the closer the molecules are and the harder the outer molecules enter the inner layer of the vesicle. So the diameter of the vesicle will not increase any more after certain salinity but decrease due to the shrinkage of the inner layer.

4. Conclusion

The mixing of anionic and zwitterionic surfactants has both the similar characters to that of oppositely charged surfactant, and the freedom of controlling the interaction between them. The proper geometry combination of the two kinds of molecules and the contribution of salt lead to the formation of a cuplike structure and ultimately the formation of vesicle. The experiments of microcalorimeter, negative-staining TEM and quasi-elastic light scattering (QELS) demonstrate the existence of vesicles in the mixture, the expansion of the vesicle formation range after adding salt and the decrease of the polydispersity with increasing salinity at the mixing ratio of 7/3. It must be noted that the formation of monodispersed vesicles will contribute greatly to the future study of vesicular catalysis, enzymatic catalysis in vesicles, etc.

Acknowledgements

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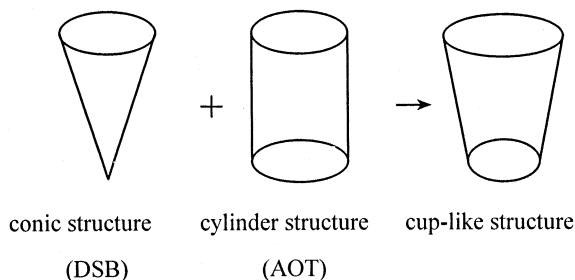


Fig. 6. Geometric structure of vesicle formation.

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