

Study on the Formation of Urea or Salt Induced Vesicles in Built-system Surfactant

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Abstract: The spontaneous formation of vesicles in the aqueous of cationic surfactant phosphate (PTA) and anionic surfactant sodium dodecyl sulfate (SDS) at certain mixing ratios have obtained¹. The addition of urea or NaI will expand the range of spontaneous vesicle formation. The fact is demonstrated by negative-staining transmission electron microscope(TEM) and dynamic light scattering(DLS) methods. The phenomenon especially in the part of urea is reported by us at first. Mechanism of urea/NaI-induced vesicles formation is discussed from the viewpoint of the molecular geometry packing parameter f , conformation and interaction.

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

Recently, many literatures have reported that spontaneous vesicle are obtained in the built-up systems of surfactants. The influences of concentration of surfactants²⁻⁶, pH^{5,7}, temperature^{1,5}, and salinity^{2,8} have also been studied. A new phenomenon of spontaneous vesicle is reported in this paper. At the certain ratio of PTA and SDS, the vesicles did not form. The vesicles have demonstrated by negative-staining TEM and dynamic light scattering.

Experimental

Tri-(dodecyldimethylhydroxypropyl ammonium chloride) phosphate (PTA), provided by the Research Institution of Jinling Petrochemical Co., was doubly purified (98.5% purity); sodium dodecyl sulfate (SDS) was obtained from Fluka Co. without any further purification (>98% purity); NaI and urea are in A.R grade.

Observation by transmission electron microscope (TEM, JEM-1200EX) was performed with a negative-staining method; the diameter and polydispersity of vesicles was determined by the dynamic light scattering method (DLS, Brookhaven Instrument C., BI-200SM goniometer and BI-900AT correlator) with an argon ion laser operating at 488 nm. All the measurement was performed at the scattering angle of 90° and 25 °C.

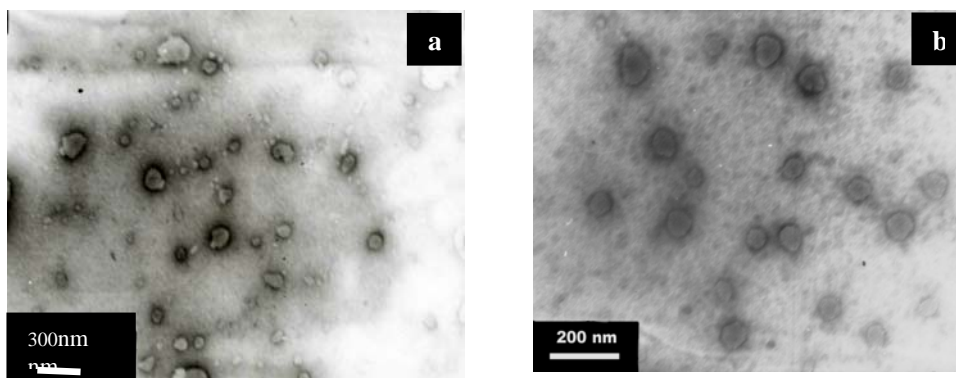
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Results and Discussion

Urea-induced vesicle self-formation

In PTA/SDS system, when the concentration of the total surfactant is lower than 0.005 mol/L and their molar ratios are 7:3; 8:2; 9:1, the mixture is colorless, the particle size of the transparent solution is about 2~3 nm. Therefore there are micelles and no vesicles. Addition of 0.05 mol/L urea to the solution at the ratio of 7:3, at the beginning no variation was observed. Several hours later, the solution became light-blue, indicating the formation of vesicles⁹. This is proved by the negative-staining TEM photos (**Figure 1a**), which showed majority of regular-shaped vesicles with diameters 100 - 150 nm, a threadlike liquid crystal was observed in the mixed solution. Under a high-speed centrifugation (2000 r/min) the solution was separated to two layers: the upper was light-blue liquid and the lower was viscous one. The lower phase appears some glittering spots between polarizing slices, indicating the presence of the isotropic liquid crystal phase. Thus, the above urea-induced solution is a coexist system of vesicle and liquid crystal. The same phenomenon was also observed when the molar ratios of PTA/SDS are 8/2 and 9/1 and the corresponding amounts of urea were added.

Figure 1 The TEM photos of vesicle induced by ure and NaI



a., urea (PTA/SDS=7/3 $C_{\text{total}} = 0.005 \text{ mol/L}$, $C_{\text{urea}} = 0.05 \text{ mol/L}$);
b., NaI (PTA/SDS = 8/2 $C_{\text{total}} = 0.0025 \text{ mol/L}$, $C_{\text{NaI}} = 0.0075 \text{ mol/L}$)

Salt-induced vesicle self-formation

We also observed that NaI could induce the vesicle self-formation, while NaCl and NaBr could not. When the molar ratio of PTA/SDA=8/2, the total concentration was 0.0025 mol/L. The diameters of micelles were 1.8~2.1 nm. When 0.0075 mol/L of NaI is added, the formation of vesicle could be observed, proved by the negative-staining TEM (**Figure 1b**). The spherical particles were uniform with the range of 30 - 100 nm. The same results were observed, when the mixed molar ratios of PTA/SDS were 7/3 and 9/1 and the same amount of NaI was added. NaCl-induced vesicle self-formation for

AOT/DSB system has also been observed in this group².

The data from DLS can obtain the size and the size distribution of the particles (**Table 1**) which indicated when the surfactant concentration is fixed, the vesicle size increased with increase of the concentration of salt or urea, and the polydispersities was from 0.2 to 0.3.

Table 1 The diameter and polydispersity of the vesicles

$C_{\text{NaI}}(\text{mol/L})^{\text{a}}$	0.005	0.006	0.007	0.008	0.009	0.01
D(nm)	93.2	99.5	108.8	117.2	127.0	144.1
Polydispersity	0.202	0.212	0.173	0.183	0.112	0.163
$C_{\text{urea}}(\text{mol/L})^{\text{b}}$	0.03	0.04	0.05	0.06	0.07	0.08
D(nm)	93.3	137.3	147.6	163.8	178.1	183.3
Polydispersity	0.257	0.294	0.295	0.247	0.282	0.469

^a surfactant concentration is fixed, 0.005 mol/L, PTA/SDS=7:3

^b surfactant concentration is fixed, 0.0025 mol/L, PTA/SDS=8:2

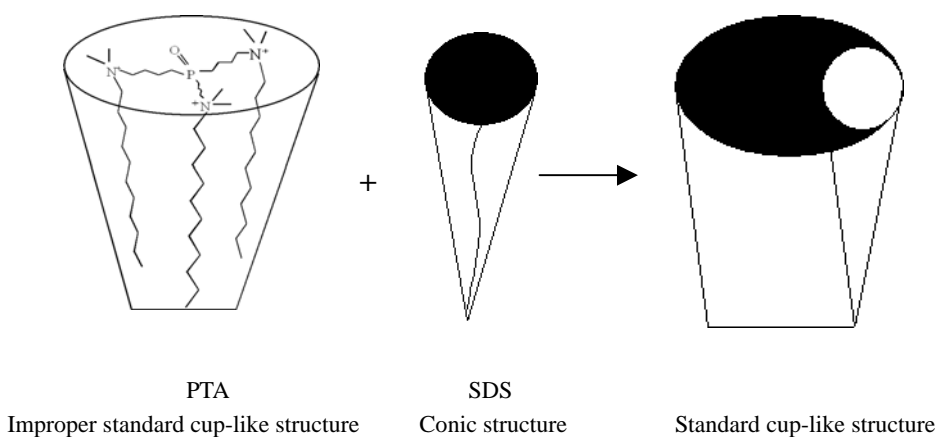
Mechanism of spontaneous vesicle formation

Tanford¹⁰ and Israelachvili¹¹ *et al.* raised that the geometric packing parameter f predicts the formation of various surfactant association structures. $f = v/a_0l_c$, where v is the particle molar volume of the hydrophobic portion of the surfactant, a_0 is the optimal head group area and l_c is the length of the surfactant tail. The structure of SDS is single head and single hydrophobic carbon-chain; the geometry of SDS molecule is conical (**Figure 2**), and $a_0 > v$, so $f < 1/2$. PTA molecule is of triammonium phosphate with three hydrophobic carbon-chains, which has a cup-like structure⁶ (**Figure 2**), and $a_0 \geq v$, so $f \leq 1/2$. On the base of Masahiko's¹² theory, we consider that the vesicle formation may due to the existance of a standard cup. PTA's cup-like can not form, only the cup-like dimmer of PTA and SDS may form vesicles (**Figure 2**).

When PTA/SDS = 9/1, 8/2, 7/3, due to the scarcity of SDS molecules, *i.e.*, the packing parameter $f < 1/2$, vesicles can not form.

The addition of salt promotes ionic strength of the system. Compressing electric double bilayer of PTA and SDS to reduce the area of hydrophilic head group is helpful for formation of the standard cup-like structure unit. Among the three kinds of halogen ionic, I ionic can easily enter the Stern layer of PTA for its large volume and strong Van der Waals force, thus can more effectively reduce diffusion potential of PTA, which can form a standard cup-like structure unit.

Urea can easily bind with water molecules through hydrogen bond and destroy structural water around hydrophilic head group and reduce its a_0 . At the same time, urea destroys the "iceberg structure" around the hydrophobic carbon-chains of the surfactant¹³. Therefore the three tails of PTA enables to extend easily and thus the volume (v) of hydrophobic carbon-chains increased. So urea enhances vesicle formation in both effects.

Figure 2 Geometric structure of surfactants and the ion-complex

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