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Spontaneous Formation of Vesicles by N-Alkyl-N-Methylmorpholinium Bromide and Sodium Dodecyl Sulfate (SDS)

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Abstract. The formation of vesicles, composed of N-alkyl-N-methylmorpholinium bromide ([Mor_{1,12}]Br) and sodium dodecyl sulfate (SDS), is investigated. The phase diagram of the mixed surfactant aqueous solutions is determined through visual observation and electrical conductivity measurements. The formation of vesicles is confirmed in the lamellar phase (L_α) through Cryo-TEM. The irregular shape of vesicles is observed successfully in micrographs. Moreover, the rheological properties, size distribution and zeta potential in different mole ratio are studied. The behavior of the vesicle solution matches Bingham fluid in rheological tests. With the mole ratio *r* increases, the average size increases while the zeta-potential value decreases. Electrostatic and hydrophobic interactions are regarded as the main driving forces for the formation of vesicles.

1. Introduction

The vesicles have aroused much interest due to their special properties and structures: hydrophilic and hydrophobic microdomains and double-layer membrane structure. Their wide applications involve drug delivery[1], biological simulation[2], and self-assembly unit of new structural materials[3]. The preparation methods of vesicles can be divided into spontaneous and external means such as ultrasonic vibration, ethanol injection and chloroform injection.[4] Without troublesome steps, spontaneous formation is widely considered to be the most simplest and most efficient method for vesicles preparation. Many studies have been published to characterize the properties and microstructure of spontaneous vesicles. Yukishige et al. found spontaneous vesicles in didodecyldimethylammonium bromide (DDAB)/sodium dodecyl sulfate (SDS) system in differential interference pictures.[5] Kaler group investigated self-assembled vesicles formed of SDS and dodecyltrimethylammonium bromide (DTAB).[6] Yuan studied the phase behavior of an aqueous catanionic surfactant system, composed of a long-chain imidazolium ionic liquid 1-dodecyl-3-methylimidazolium bromide (C₁₂mimBr) and sodium dodecyl sulfate (SDS). Through optical photographs combined with electricity conductivity tests, a birefringent L_α phase is usually observed with vesicles exist.[7]

As previously reported, the mixtures of cationic and anionic surfactants have been employed to form vesicles due to electrostatic. Since the morpholine bromide has favorable properties such as simple mechanism in synthetic, cheaper cost and good ionic conductivity, it has been widely used in organic synthesis, thermodynamics and pharmacy. It is suitable for using as a cationic surfactant to form the vesicles with SDS.

In this work, the vesicle formation and phase behavior of [Mor_{1,12}]Br/SDS system are studied. The



phase diagram of the mixed surfactant aqueous solutions is determined through visual observation and electrical conductivity measurements. The formation of vesicles is confirmed in the lamellar phase (L_a) through Cryo-TEM. The irregular shape of vesicles is observed successfully in micrographs. Moreover, the rheological properties, dynamic light scattering and zeta potential in different mole ratio are studied. Electrostatic and hydrophobic interactions are regarded as the main driving forces for the formation of vesicles. This work is expected to be a good supplement to the self-assemble science especially for mechanism of vesicle formation.

2. Experimental Section

2.1. Materials

The N-alkyl-N-methylmorpholinium bromide ($[\text{Mor}_{1,12}]\text{Br}$) was synthesized in our laboratory as described previously.[8] Sodium dodecyl sulfate (SDS) was purchased from Aladdin Chemistry Co. Ltd. Deionized water was used throughout the work.

2.2. Methods

A concentration of 100 mM N-alkyl-N-methylmorpholinium bromide was prepared with deionized water. Various concentration of SDS were added into the N-alkyl-N-methylmorpholinium solution (10mL). The mole ratio r [$r = n(\text{SDS}) : n(\text{N-alkyl-N-methylmorpholinium})$] was varied from 0 to 1. The phase behavior was reported by photos and the phase regions were determined by conductivity measurements.

2.3. Equipments

Electrical conductivity measurements were carried on DDS-307 (Shanghai Precision & Scientific Instrument Co., Ltd.). Rheological measurements of the $[\text{Mor}_{1,12}]\text{Br}/\text{SDS}$ system was characterized by Haake Mars 60 rheometer. The hydrodynamic radius distribution and zeta potential of the vesicles was obtained by the NanoBrook Omni Laser particle size analyzer. The temperature of all tests above was set at 25°C.

3. Results and Discussion

3.1. Phase behavior of the $[\text{Mor}_{1,12}]\text{Br}/\text{SDS}$ aqueous solution

The different concentration of anionic surfactant SDS is added into $[\text{Mor}_{1,12}]\text{Br}$ aqueous solution (100mM), with the molar ratio r ($r = n(\text{SDS}) : n([\text{Mor}_{1,12}]\text{Br})$) ranges from 0 to 1. Different phases in the mixture are shown in Figure 1.

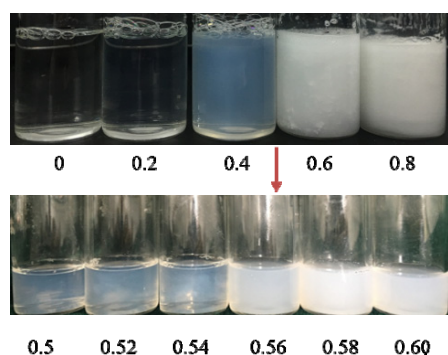


Figure 1. Photographs of the aqueous $[\text{Mor}_{1,12}]\text{Br}/\text{SDS}$ system with the increasing molar ratio r .

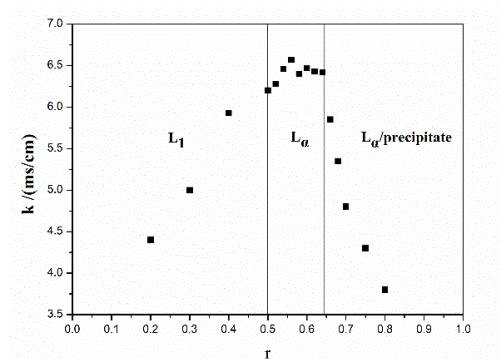


Figure 2. A phase diagram of the $[\text{Mor}_{1,12}]\text{Br}/\text{SDS}$ system with varied mole ratio r .

A series of phase changes are observed with the mole ratio r varied from 0 to 1. The phase behavior of system changes from lightly bluish to turbid white with the increase of r (the amounts of SDS). It can be observed that with r between 0 and 0.4, a transparent and low-viscosity solution is observed, regarded as L_1 phase (micellar solution). With r ranges between 0.4 and 0.5, a slightly bluish solution is observed.

A turbid bluish solution appears with r between 0.5 and 0.56, it is called L_α phase. Vesicles generally exist in L_α phase. In order to get more information about vesicles, electrical conductivity measurements are employed to investigate phase behavior of the mixture.

Figure 2 represents the electricity conductivity of $[\text{Mor}_{1,12}]\text{Br}/\text{SDS}$ system. when r is between 0 and 0.5, k increases greatly. L_1 phase (a micellar solution) can be found with slightly bluish and low-viscosity in visual observation. As r increases from 0.5 to 0.64, k changes slightly. A bluish L_α phase is observed in this period, the vesicles existed in this phase.[9, 10] This has been confirmed in section 3.3 by Cryo-TEM measurements. For solutions with r between 0.64 and 0.8, k decreases steeply in L_α /precipitate phase. To further confirm vesicles in the L_α phase, a Cryo-TEM measurement is used. Figure 5 shows a microstructure of $[\text{Mor}_{1,12}]\text{Br}/\text{SDS}$ system (100 mM $[\text{Mor}_{1,12}]\text{Br}$ and $r=0.52$).

3.2. Formation of vesicles in the L_α phase

3.2.1. Rheogram of the oscillatory shear parameters of the birefringent L_α phases. The macroscopic properties of $[\text{Mor}_{1,12}]\text{Br}/\text{SDS}$ solution is studied by rheogram method. The vesicle system with $r=0.52$ is taken as an example. As illustrated in Figure 3(a), the storage modulus G' is about 1.0 mPa and the loss modulus G'' is about 0.1 mpa. The two parameters keep more or less constant, representing elastic and viscous properties are almost stable. And the G'' is one order of magnitude bigger than G' , vesicles are dominated by the viscosity behavior.

From Figure 3(b), the complex viscosity $|\eta^*|$ decreases from 4.5 to 11.3 pas with the increase of frequency. The results all above indicate that the behavior of the vesicle solution matches Bingham fluid, it is the same with other aqueous catanionic mixtures.

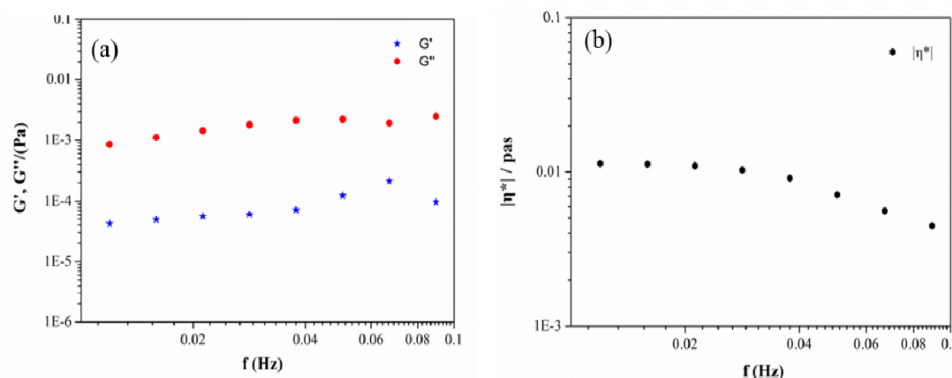


Figure 3. Rheogram of the oscillatory shear parameters of sample (100 mM $[\text{Mor}_{1,12}]\text{Br}$ and $r=0.52$)

3.2.2. Size distribution and zeta potential. DLS is obtained to characterize the size distribution of the $[\text{Mor}_{1,12}]\text{Br}/\text{SDS}$ system, and the zeta potential is used to investigate the stability of colloid solutions. The results are shown in Figure 4 and Table 1. From Figure 4, the average size of vesicles ($r=0.52$) is 162.3 nm. These particles have a polydisperse size distribution, which is in accordance with the Cryo-TEM results.

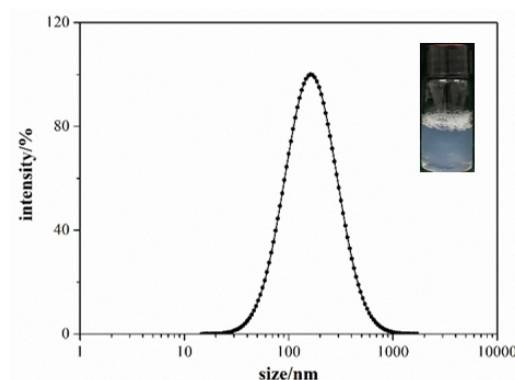


Figure 4. Hydrodynamic radius distribution of mixed surfactant (100 mM $[\text{Mor}_{1,12}]\text{Br}$ and $r=0.52$)

Table 1. Average size and zeta-potential values of sample with different r

r	0.5	0.52	0.54	0.56	0.58	0.60
Average size/nm	124.8	162.3	253.4	522.7	1308.5	1727.7
Zeta-potential/mv	16.7	13.0	11.5	8.4	6.7	3.2

In the same charged environment, the larger the absolute value of the zeta potential, the more stable the system.[11] From Table 1, with the increase of the amounts of SDS (r), the average size of particles in aqueous solution increases, while the zeta potential decreases in the overall trend. In the range of 0.5-0.6 of r , vesicles with smaller r are more stable.

3.3. Possible formation mechanism of the vesicles in the $[\text{Mor}_{1,12}]\text{Br}/\text{SDS}$ systems

To investigate the microcosmic characteristic of vesicles in the $[\text{Mor}_{1,12}]\text{Br}/\text{SDS}$ systems, Cryo-TEM measurements are employed. The concentration of $[\text{Mor}_{1,12}]\text{Br}$ is 100 mM and the mole ratio of SDS to $[\text{Mor}_{1,12}]\text{Br}$ is 0.52. Figure 5 shows the micrographs of the densely distributed vesicles, and their sizes are range from 80 to 200 nm, which confirms the results of DLS tests. Dense arrangement and extrusion produce viscoelasticity. When r is 0.52, cationic surfactant ions $[\text{Mor}_{1,12}]^+$ are excessive. As a result, the bimolecular layer has a positive surface charge. The electrostatic repulsion increases the interlayer spacing of vesicles, and unilamellar vesicles are formed.

The driven forces are electrostatic and hydrophobic interactions. [12] In the mixtures of cationic and anionic surfactants, $[\text{Mor}_{1,12}]^+$ and DS^- form ion pairs due to the electrostatic interaction. The ion pairs form aggregates which grow into vesicles because of hydrophobic interactions.

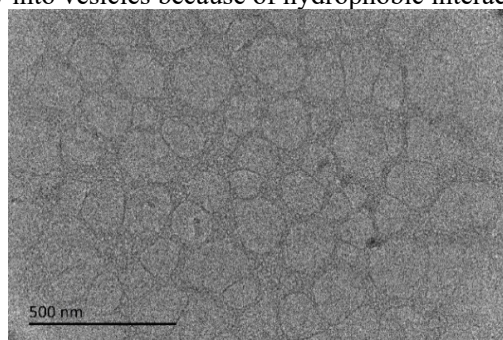


Figure 5. Cryo-TEM micrograph of the $[\text{Mor}_{1,12}]\text{Br}/\text{SDS}$ system

4. Conclusion

In this work, the vesicle formation of N-alkyl-N-methylmorpholinium bromide ($[\text{Mor}_{1,12}]\text{Br}$) and SDS system is investigated. L_α phase is observed through visual observation and electrical conductivity measurements when the mole ratio r ranges from 0.5-0.6. Micrographs are obtained by Cryo-TEM to confirm the existence of vesicles in the L_α phase. The densely distributed vesicles are observed and

their sizes are between 80-200 nm. The larger the amounts of SDS, the larger particle sizes. The rheogram results indicate that the behavior of the vesicle solution matches Bingham fluid. Through the simple work, the driven forces for the formation of vesicles are electrostatic and hydrophobic interactions.

Acknowledgments

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