

Microscopic Study of AOT and CTAB Anionic-rich Catanionic Phase

(Kajian Mikroskopik Anionik-kaya dalam Fasa Katanionik AOT dan CTAB)

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ABSTRACT

Catanionic system using anionic sodium bis-(2ethylhexyl)sulfosuccinate (AOT) and cationic cetyltrimethylammonium bromide (CTAB) is studied. The system is prepared by addition of CTAB solution to a prepared AOT solution until slight anionic-rich catanionic phase is produced. Catanionic system consists of the mixture of different types of surfactants and counterion due to electrostatic interaction between the oppositely charged surfactant. Both of these products affect the in surface activity of the surfactant. Hydrodynamic diameters decrease and clearer solution were seen with the increase of CTAB concentration in solution mixture. As a result, mixed surfactant with larger hydrophobic region and the presence of counterion will induce smaller vesicle to form in catanionic system.

Keywords: Alkyl chain number; anionic-rich phase; catanionic system; electrostatic interaction; surfactant number

ABSTRAK

Sistem katanionik dengan menggunakan anionik natrium bis-(2etilheksil)sulfosuccinat (AOT) dan kationik cetiltrimetilammonium bromida (CTAB) telah dikaji. Sistem ini disediakan melalui penambahan larutan CTAB kepada larutan AOT yang disediakan sehingga fasa kationik yang beranionik terhasil. Sistem kationik ini mengandungi dua jenis surfaktan yang berbeza dan garam disebabkan kewujudan interaksi elektrostatik pada perbezaan cas dalam surfaktan. Bahan hasilan ini memberi kesan kepada aktiviti permukaan surfaktan. Garispusat hidrodinamik menurun dan larutan menjadi jernih dengan penambahan kepekatan CTAB kepada larutan AOT. Kesimpulannya, hasil surfaktan baru dengan bahagian hidrofobik yang lebih besar dan garam akan mempengaruhi vesikel yang kecil terbentuk dalam sistem katanionik.

Kata kunci: Fasa anionik-kaya; interaksi elektrostatik; nombor rantai alkil; nombor surfaktan; sistem katanionik

INTRODUCTION

Molecular attractions between oppositely charged surfactants in cationic and anionic surfactant mixture in catanionic systems are rather strong compared to other systems due to electrostatic interaction. These catanionic systems promote spontaneous vesicle formation, first introduced by Kaler et al. (1989), exhibits similar phase behaviour in lipids (Marques et al. 2003) and provides good stability (Chen et al. 2004). It was reported that vesicle states change in catanionic systems upon heating, which would induce vesicle fusion and growth (Andreozzi et al. 2010). Therefore, catanionic vesicles are said to be fascinating objects justifying abundant research works (Tondre & Caillet 2001). With these great advantages, studies on catanionic systems and vesicles had been widely done (Fuangswasdi et al. 2006a, 2006b; Hao et al. 2006; Marques et al. 1998; Tah et al. 2011). In addition, anionic-rich catanionic system have been reported to be thermodynamically stable (Marques et al. 1998) and better in glucose encapsulation (Fischer et al. 2002) compared to cationic-rich system.

There are limited reports on catanionic systems involving sodium bis-(2ethylhexyl) sulfosuccinate (AOT) and cetyltrimethylammonium bromide (CTAB).

However, there is a report to determine the critical micelle concentration of AOT/CTAB system where the authors reported that precipitation occurred at CTAB mole fraction between 0.3 and 0.7 (Zheng et al. 1995).

In this work, we prepared the catanionic mixture using CTAB and AOT forming a phase from concentrated anionic solution to slight anionic-rich catanionic system. We investigated the catanionic solution by observing turbidity, correlating both visually and uv-vis transmission measurement. Microscopic-scale measurements were made using polarized light microscope and dynamic light scattering to examine the reaction after anionic solution were added with cationic solution.

EXPERIMENTAL DETAILS

MATERIALS AND PREPARATION

The surfactant bis-(2-ethylhexyl)sulfosuccinate (Aerosol OT/AOT, 98%, Sigma) and N-cetyl-N,N,N-trimethylammonium bromide (CTAB, 98%, R&M Chemicals) were used without further purification. Both CTAB and AOT solutions were prepared using a simple hydration method using ultra pure water (Maxima Ultra

Pure Water, Elga-Prima Corp, UK) with a resistivity of 18 M Ω /cm. Both solutions were heated to 45°C and were further vortex shaken. Catanionic solutions at different molar ratio (R) were prepared as showed in Table 1, with an AOT solution as a standard comparison. Samples were immediately characterized after the mixtures are homogenized by mechanical vortex.

CHARACTERIZATION ON CATANIONIC SOLUTION

Vesicle diameter, size distribution and polydispersity values were measured using the computerized dynamic light scattering (DLS), Malvern Zetasizer, Nano ZS (Malvern Instruments Ltd., England) equipped with a 4 mW helium neon laser with a wavelength output of 633 nm. The intensity autocorrelation functions were calculated using DTS software in the computerized DLS system. As for the solution turbidity, it was observed and measured by transmission spectrum of the samples using a computerized Lambda 35 UV/VIS Spectrophotometer (PerkinElmer). Light intensity passing through the solutions was calculated using UV WINLAB software. Each sample was placed into a disposable cuvette. All measurements were performed at 25°C. In addition, vesicle presence was confirmed by the appearance of a Maltese Cross under polarized light microscope. A few drops of solution were settled onto a microscope glass slide and observed under polarized microscope (Meiji Techno ML9300 Series, 4 \times magnification). The observed images were captured at room temperature using a mounted Nikon CoolPix 995 digital camera with the same magnification.

RESULTS AND DISCUSSION

GENERAL APPEARANCE OF MIXTURES AOT AND CTAB

AOT is a gel-based surfactant where the addition of heat and mechanical vortex are needed to homogenize the solution. AOT and CTAB catanionic system are mixed at each ratio. The appearance of each solution at different ratio was examined visually after addition of CTAB solution to standard AOT solution. Table 1 shows the visual observable characteristics (appearance of turbidity) for each solution. The observed solutions were first very turbid for the AOT solution and similar to the surfactant mixture for all R except for 16:1, which had a more transparent appearance. In addition, light intensity transmitted through the solutions for turbidity measurement was also collected for 4 of the samples, AOT solution and solutions at R of 200:1, 80:1 and 16:1, as shown in Figure 1.

INFLUENCE TO STANDARD SOLUTIONS

The effect of CTAB solution on AOT solution was investigated using a polarized light microscope to observe vesicle, presents as a Maltese Cross. Figure 2 shows the polarized image of the AOT solution, R at 400:1, 200:1 and 16:1. Figure 2(a) is a polarized light image of standard AOT solution, vesicles around 30 μ m in diameter were observed. After addition of CTAB to the standard solution into the appropriate ratios, vesicles are still visible but counts are reduced for both R at 400:1 and 200:1 (Figure 2(b) and Figure 2(c), respectively) of catanionic solution. However,

TABLE 1. Visible characteristics of solutions at different R of [AOT]/[CTAB]

R (mol : mol)	AOT	400:1	200:1	150:1	80:1	50:1	16:1
Appearance	Turbid	Turbid	Turbid	Turbid	Turbid	Turbid	Clear

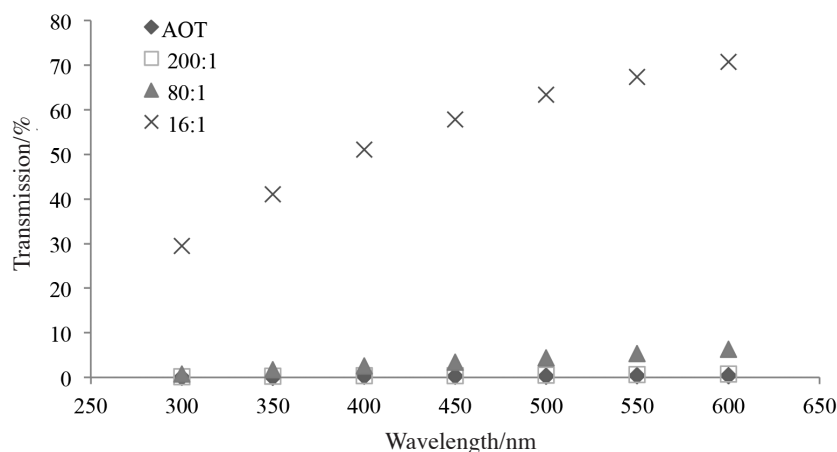


FIGURE 1. Light transmission (in percentage) detected in ultra-violet and visible light region. For AOT solution, R at 200:1 and 80:1 has less than 10% transmission detected

for Figure 2(d), with R at 16:1, vesicle was less visible or forming at a smaller scale that is unable to observe clearly under the microscope.

Hydrodynamic diameters for each solution were measured and analyzed by light scattering as shown in Figure 3. Table 2 shows the values of the average hydrodynamic diameter as well as the polydispersity values for AOT solution, catanionic solutions at R of 200:1, 80:1 and 16:1. After the CTAB addition, diameter decreased from average of over 800 nm in AOT solution to 140 nm in the catanionic solution. The AOT solution shows the highest polydispersity value of 0.792. In addition, AOT solution showed three broad hydrodynamic diameters around 10, 60 and 400 nm whereas the distribution of diameters for the solution with R at 16:1 has smaller peak within 10 - 100 nm and a broader peak, ranging from 100 to 700 nm (Figure 3).

INTERACTION BETWEEN SURFACTANTS

It is known that turbidity of the solution is caused by the formation of multilamellar vesicles (MLV). So, turbid in AOT solution would suggest the presence of high bilayer number vesicle or MLV formation due to short chemical structure of 6 alkyl chains. After CTAB solution addition, catanionic solution of 16:1 showed higher light transmission percentage than others (Figure 1). The clearer solution appearance was due to decrease in bilayer numbers or suggested to be the presence of unilamellar vesicles (Feitosa et al. 2006). Indeed, under polarized light microscope, fairly standard sizes of giant multilamellar

vesicle (30 μm) were observed in AOT solution and R of 400:1. Similarly, vesicles measuring 40 μm also being observed in DDAB/SDS mixture (Kondo et al. 1995). Two peaks in diameter distribution measurement were detected in mixture 16:1. The smaller peak is within 10 - 100 nm was suggested to be both and different micellar formation (Marques et al. 1998) from each surfactants whereas the broader peak, ranging from 100 to 700 nm suggested to be micelle-vesicle co-existence (Velázquez et al. 2007)

The existence of opposite charged surfactant caused a reaction between counterions, forming sodium bromide salt (Br^- from CTAB and Na^+ from AOT, respectively) and a mixed charged-free surfactant. As R decreases from 400:1 to 16:1, higher concentration of counterions were produced. Counterions or salts will increase the surfactant packing parameter and highly induce surfactant aggregates (Marques et al. 1998). Hence, induce the formation of smaller scale of vesicles.

ALKYL CHAINS IN CATANIONIC SYSTEM

With a higher total surfactant concentration, the average hydrodynamic diameter for R at 16:1 was 137.8 nm, slightly lower than that reported by Chen et al. (2004) at 324.6 nm, who used tri-(*N*-dodecyldimethylhydroxypropylammonium chloride) Phosphate, PTA cationic surfactant in AOT/PTA system with 5:5 ratio. The main differences between Chen et al. (2004) and the current study is the surfactants' alkyl chain numbers. Anionic AOT were used in both of the system. However, for the opposite charged, cationic CTAB with a alkyl tail, compared with poly-tailed

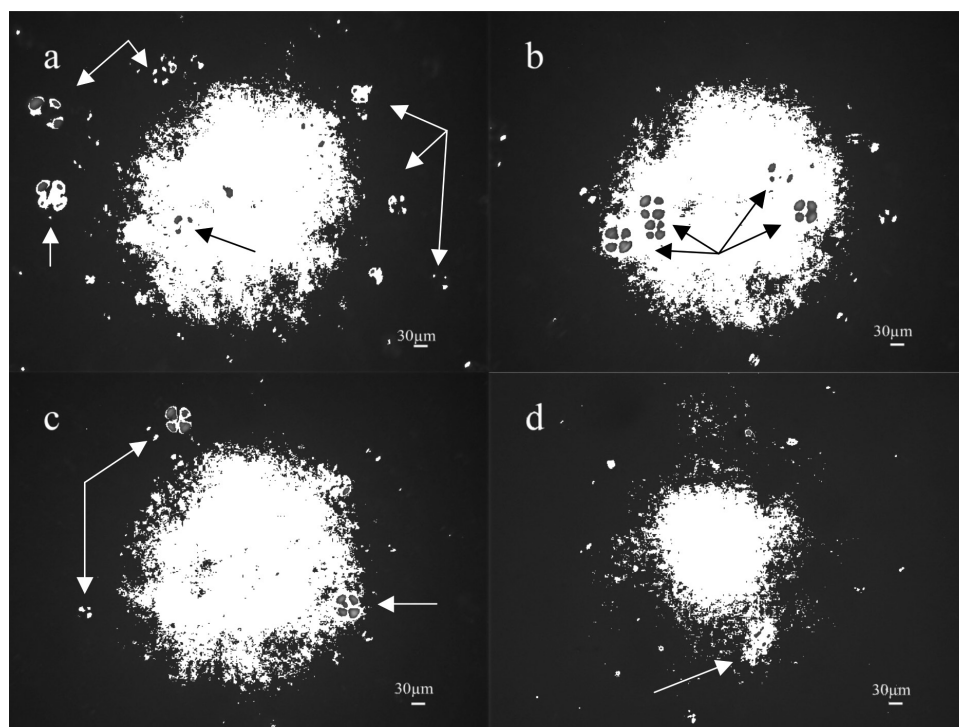


FIGURE 2. Vesicles appearing as a Maltese Cross (arrows) under polarized light microscope for standard AOT solution (a) and different R of 400:1 (b), 200:1 (c) and 16:1 (d) solutions. (Bar = 30 μm)

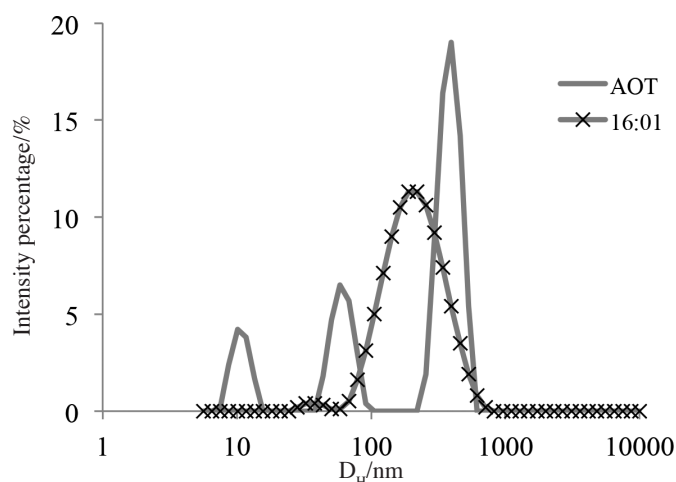


FIGURE 3. Hydrodynamic diameter distributions for AOT solution and mixture at R =16:1(cross). All samples are measured at 25.0°C

TABLE 2. Average hydrodynamic diameters and polydispersity values for AOT solution and catanionic solutions with respective R

R (mol:mol)	Z-average diameter (D_H ,nm)	Polydispersity value
AOT solution	838.9	0.792
200:1	297.7	0.415
80:1	182.3	0.238
16:1	137.8	0.370

PTA, had lesser surface activity (Jurašin et al. 2010) among surfactants' molecule. Thus AOT/CTAB system has a smaller average diameter compared to AOT/PTA system. On the other hand, our results showed similar decreasing in average hydrodynamic diameter with SDS/CTAB anionic-rich catanionic system (Andreozzi et al. 2010) from ratio 2.5:1 to 1:1.

In addition, mixing 2 oppositely charged surfactant in this report will induce formation of a surfactant with 3 alkyl chains due to electrostatic interaction. Schematically showed in Figure 4, negatively charged surfactant with 2 alkyl chain incorporate with single tail cationic

surfactant. The product surfactant, with 3 alkyl chain and no charged, will increase in surface activity and biased towards formation of vesicle (Marques et al. 1998) at the range of 100 to 700 nm at ratio of 16:1, from 2 small peak (ranging ~10 nm and 80 – 100 nm) in AOT solutions as in Figure 3. Surfactant number is $v / a_0 l_c$, where v is the volume of the hydrophobic portion of the surfactant, l_c is the length of the hydrophobic group, and a_0 is the area of the hydrophilic head group. Mixed surfactant has significant increase in hydrophobic portion, v , due to increase in alkyl chain will thus increase the surfactant number that will promote the formation of vesicles.

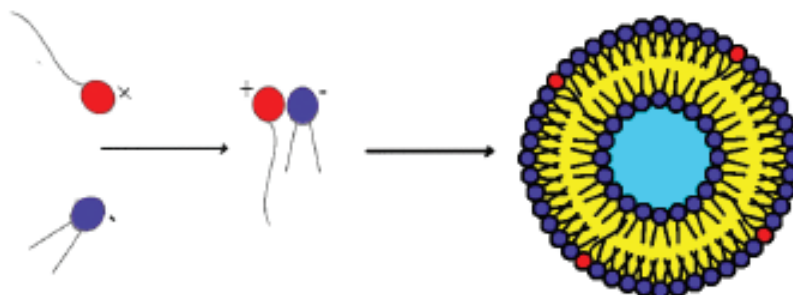


FIGURE 4. Schematic drawings of mixed surfactant type due to polar interactions of oppositely charged surfactants and further formation as catanionic vesicles

CONCLUSION

AOT/CTAB catanionic system was prepared and analyzed using light scattering, polarized microscopy and uv-vis spectrometer for hydrodynamic diameter, vesicle appearance and visual appearance and transmission intensity. Catanionic system was prepared from anionic solution to slight anionic-rich phase. The images from polarized microscope for AOT solution shows vesicles around 30 μm , a fairly standard diameter known. The images show less vesicle count after CTAB added, while solution turbidity become clearer correlated between vesicle size and solution turbidity. On the other hand, the average hydrodynamic diameter measured in range of 140- 850 nm. The continual addition of CTAB will induce formation of mixed surfactant consist of both AOT and CTAB molecules. The resultant surfactants will increase the production of counterion and larger portion of hydrophobic regions. Both increases in counterion and hydrophobic regions will greatly increase in surfactant number which will highly promote the formation of catanionic vesicle.

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