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Edy Giri Rachman Putra and Arum Patriati

Structural and Phase Transition Changes of Sodium Dodecyl Sulfate Micellar Solution in Alcohols Probed by Small-Angle Neutron Scattering (SANS)

Edy Giri Rachman Putra[a] and Arum Patriati[a,b]

[a]Neutron Scattering Laboratory, National Nuclear Energy Agency of Indonesia (BATAN),
Gedung 40 BATAN, Kawasan Puspiptek Serpong, Tangerang 15314, Indonesia
[b]Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Gadjah Mada,
Bulaksumur, Yogyakarta 55281, Indonesia
giri@batan.go.id

Abstract. Small-angle neutron scattering (SANS) measurements on 0.3M sodium dodecyl sulfate (SDS) micellar solutions have been performed in the presence of *n*-alcohols, from ethanol to decanol at different alcohol concentrations, 2-10 wt%. The ellipsoid micellar structure which occurred in the 0.3M SDS in aqueous solution with the size range of 30-50 Å has different behavior at various hydrocarbon chain length and concentration of alcohols. At low concentration and short chain-length of alcohols, such as ethanol, propanol, and butanol, the size of micelles reduced and had a spherical-like structure. The opposite effect occurred as medium to long chain alcohols, such as hexanol, octanol and decanol was added into the 0.3M SDS micellar solutions. The micelles structure changed to be more elongated in major axis and then crossed the critical phase transition from micellar solution into liquid crystal phase as lamellar structure emerged by further addition of alcohols. The inter-lamellar distances were also depending on the hydrocarbon chain length and concentration of alcohols. In the meantime, the persistent micellar structures occurred in addition of medium chain of *n*-alcohol, pentanol at all concentrations.

Keywords: small-angle neutron scattering, micellar solution, micelles, liquid crystals, lamellar structure.
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INTRODUCTION

The size and structure of ionic micelle aggregates containing commonly used surfactants and co-surfactants in aqueous solution have been intensively studied in the last several years. It has been well known that the micellar sizes and structures depend on the ionic strength and on the amphiphilic concentration as a result of the balance between hydrophobic and hydrophilic (electrostatic) forces among ionic surfactant molecules on the self-association and formation of micelles [1]. This leads in minimizing the degree of mixing between hydrophobic tails of surfactant and water molecules, and then the hydrophobic head-groups are in contact with the water.

One of the most interesting aspects of micelles is their ability in enhancing the solubility of different immiscible organic molecules into a macroscopically homogeneous single phase [2-4]. An increased flexibility of the micellar membrane and thereby an improved ability to solubilize hydrophobic molecules

can be achieved by changing the ionic strength of solution through salts or additives addition. Therefore, ionic micelle aggregates has a wide range of application such as in the formation of microemulsions for ternary oil recovery, detergency, cosmetics, printing, drug-delivery system and dyeing, synthesis of mesoporous materials, catalysis and as templates for nanostructures [5-7].

Sodium dodecyl sulfate (SDS) micellar solution was commonly used as a model of micellar structure for understanding the self-association and aggregation of SDS molecules by modifying the solution properties. Addition of NaCl in 0.3M SDS micellar solutions increased the micellar size and promoted a structure transition from spherical-like into rod-like (worm-like) shape micelles [8]. The present of salt reduced the repulsion force between sulfate head groups and then decreasing of packing parameter to reach a minimum free energy on micellization. While addition of co-surfactant of carboxylate acid, i.e. lauric and palmitic acids and non-polar organic molecules, i.e. hexane,

octane, and decane in 0.3M SDS micellar solutions has shown complicated behaviors of micellar structure [9]. This problem is caused by a delicate balance of attractive and repulsive forces among the amphiphilic molecules in the micelles.

The effect of short to medium chain-length n-alcohol molecules in low to medium concentration of SDS micellar solutions has been studied previously [10-13]. Those studies showed that the modified solvent by addition of short chain n-alcohols affected the micellization process. While medium chain n-alcohols also affected the micellar structure by assembled the alcohol molecules in the micelle aggregates. However, the roles of the amphiphilic n-alcohol molecules as co-surfactants are still unclear and a matter of discussion especially at high concentration micellar solutions and long chain n-alcohols.

In order to clarify some problems concerning the effect of n-alcohols on the behavior of SDS micelles, this paper reports a study of micellar structure of SDS micelles in the presence of various amounts of ethanol, propanol, butanol, petanol, hexanol, octanol and decanol. The concentration of free salts SDS micellar solution was fixed at 0.3M and the n-alcohols concentration varied from 2-10 wt%. Small-angle neutron scattering (SANS) technique was employed in this study to characterize the structural change of micelles in micellar solutions in nanometer scale range up to 10 nm in diameter. The Information on the average size and its distribution, spatial correlation, as well as shape and internal structure of micelles can be obtained from SANS scattering intensity profiles analysis.

In general, SANS is an important technique in order to study both the structural and dynamical properties in the range scale from 1 – 100 nm of wide range of substances in soft matters (polymers, liquid crystals, micellar solutions, microemulsions, colloidal suspensions, membranes, vesicles, proteins, enzymes, etc.), and hard matters (ceramics, alloys, amorphous materials, etc.)

MATERIALS AND METHOD

Reagents

Analytical grade of SDS and 99.9% deuterium oxide (D_2O) were purchased from Sigma-Aldrich. While the n-alcohols for synthesis grade were provided from Merck and Sigma-Aldrich. Those chemicals were used without further purification. D_2O was used as a solvent to enhance the contrast for SANS experiment by reducing the incoherent scattering of H_2O (background) where the neutron cross section of H_2O and D_2O are -0.56×10^{-10} cm^{-2} and 6.41×10^{-10} cm^{-2}, respectively. At fixed 0.3M SDS micellar solutions, various amounts of n-alcohols were added with 2-10 wt% solution concentration.

SANS Measurements

SANS experiments were carried out on SMARTer, the 36 meter SANS BATAN spectrometer at neutron scattering laboratory (NSL) in Serpong, Indonesia. The detail of the SANS BATAN spectrometer was described in other references [14-15]. Each sample was measured at two detector distances, 1.5 and 3 m, to cover a momentum transfer Q range from 0.02 to 0.25 $Å^{-1}$ with the neutron wavelength λ of 3.9 Å. The 5 mm thick of sample is contained in the quartz cell and then exposed to neutron beam for 1 hour. Meanwhile, 2 mm thick of highly viscous solution samples were prepared using aluminum special cell. During the experiment, the temperature was held at ambient temperature (25 °C). Scattering intensities of the samples are corrected for incoherent scattering; i.e. background of detector, quartz cell or aluminum cell and solvent scattering; and sample transmission by GRAPS data reduction program [16].

Data Analysis

The intensity $I(Q)$ of small-angle scattering as a function of Q, for a monodisperse interacting micelle system can be expressed as

$$I(Q) = n\left(\rho_m - \rho_s\right)^2 V^2 P(Q) S(Q) \qquad (1)$$

where n denotes the number density of micelles, ρ_m and ρ_s are the scattering length densities of the micelle and the solvent, respectively. The term $(\rho_m - \rho_s)^2$ is called contrast factor. V is the volume of a micelle. The aggregation number N of the micelle related to the micellar volume V by the relation $V = N.v$, where v is the volume of a surfactant monomer. For ellipsoid and cylinder shape it is calculated by $N = 4\pi R_a 2R_b/3v$, where R_a and R_b are respectively minor and major axis.

$P(Q)$ is the intra-particle structure factor and depends on the shape and size of the particles. $S(Q)$ is the inter-particle structure factor and is determined by the inter particle distance and the particle interaction. For ellipsoid micelle with two equal semi-axis, R_a and principal axis $zR_a=R_b$ where $R_a=R_c$, $P(Q)$ is formulated by

$$P_{el}(Q) = \int_0^{\pi/2} \left[j_1(x)\right]^2 \sin \beta \, d\beta \qquad (2)$$

where $x = Qa[\cos^2 \beta + z^2 \sin^2 \beta]$ and β is the angle between the scattering vector and the direction of the symmetry axis of ellipsoid. It is noted that $z > 1$ or $z <$

1 depending on whether the particle is prolate or oblate ellipsoids. Meanwhile, for isotropic system $S(Q)$ can be written as,

$$S(Q) = 1 + 4\pi n \int \left[g(r) - 1 \right] \frac{\sin Qr}{Qr} r^2 dr \quad (3)$$

where $g(r)$ is the radial distribution function, a probability of finding another particle at a distance r from a reference particle centered at the origin.

The corrected data was then analyzed by a screen coulomb model provided by NIST data analysis program [17]. Here, it is determined the fractional charge α and the major axis, since the minor axis is fixed at 14.3 Å, which is smaller than the length of a fully extended hydrophobic chain of SDS molecule, 16.7 Å based on the Tanford's formulation [18].

1-butanol as a function of its concentrations are shown in Figure 1. Strong correlation peak of the structure factor $S(Q)$ is already observed in the SANS profiles from the pure 0.3M SDS micellar solutions (0% alcohols). The peak at $Q_{max} = 0.086\text{Å}^{-1}$ indicates the interacting charged micelles in the solution [19] with a distance of 73Å by a relation $Q_{max} \sim 2\pi/d$, where d is the average distance between micelles. A uniform ellipsoid-structure model calculation well fitted with the experimental data. From that model, the minor R_a and major R_b axes were obtained respectively 14.3 and 21.3Å (axial ratio = 1.49) with a charge α of 30.5. The micelle structural parameters of the micelles in various amounts of alcohols at low concentration verified after a detailed analysis using a uniform ellipsoid-structure model calculation with a fixed minor axis, $R_a = 14.3$ Å is given in Table 1.

RESULTS AND DISCUSSION

The SANS distribution profiles for the first three short chain of alcohols, i.e. 1-ethanol, 1-propanol and
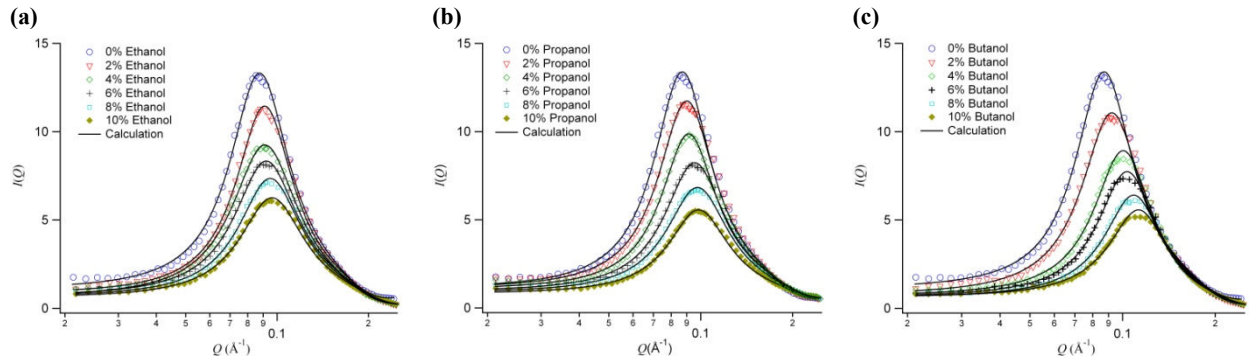

FIGURE 1. SANS scattering profiles of 0.3M SDS micellar solution in addition of short chain alcohols (a) 1-ethanol, (b) 1-propanol and (c) 1-butanol up to 10 wt% concentration, indicated in the graphs. The symbols represent experimental data and the solid line represents theoretical calculation.
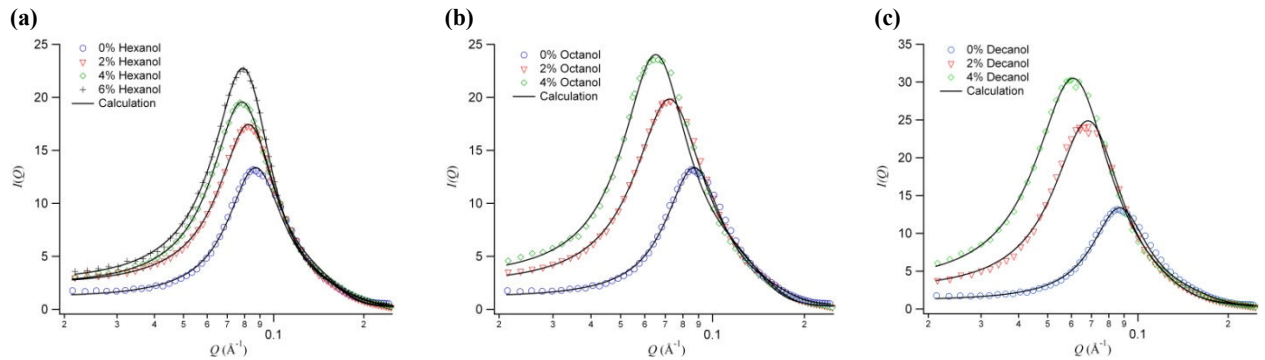

FIGURE 2. SANS scattering profiles of 0.3M SDS micellar solution in addition of short chain alcohols (a) 1-hexanol, (b) 1-octanol and (c) 1-decanol at low to medium concentrations, indicated in the graphs. The symbols represent experimental data and the solid line represents theoretical calculation.

Figure 1 clearly shows the reducing of the scattering intensity and the shifting of the correlation peak to a higher Q range by the increase of the alcohol concentrations. Meanwhile, opposite effect occurred as medium to long chain alcohols, i.e. 1-hexanol, 1-octanol and 1-decanol were added into the 0.3M SDS micellar solutions, Figure 2. The scattering intensity increased and the position of the correlation peak shifted to a lower Q range by increasing the alcohol concentrations.

From Figures 1 and 2 clearly show that the alcohol induces the structure of SDS micelle by modifying the solvent properties for soluble alcohols and reducing the contact of water molecules from the hydrophobic chain for insoluble alcohols in aqueous solution. Short-chain alcohols, up to propanol mainly dissolved in the aqueous phases and it caused destabilized the micelle thermodynamically and kinetically [11]. As a consequence, the micelles break down and form small micelles. This micelle has a propensity to be more spherical with the addition of alcohols where the axial ratio declines gradually from 1.49 (no alcohols) to about 1.13 in 10 wt% of 1-butanol, Table 1. The average distance among the micelles also decreased to about 55 Å. Nevertheless, medium- to long-chain alcohols, from hexanol to decanol certainly are immiscible in the aqueous phases and they perform unlikely as a short-chain alcohol behavior. The addition of these alcohols increases gradually the axial ratio up to about 2.2 in 4 wt% of 1-decanol, Table 1, because of solubilization alcohol molecules in the hydrocarbon interior of micelles. Along with this change, the average distance among the micelles increased to about 100 Å.
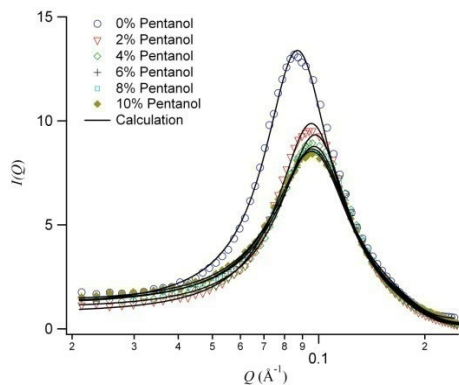

FIGURE 3. SANS scattering profiles of 0.3M SDS micellar solution in addition of medium chain alcohol, 1-pentanol up to 10 wt%. The symbols represent experimental data and the solid line represents theoretical calculation

In spite of those experimental results, the addition of 1-pentanol occurred in different manner, Figure 3. Addition of 2 wt% pentanol caused the micellar structure changed significantly like a short chain alcohol behavior. Solubilized of 1-pentanol molecules in aqueous phase had modified the solvent structure. The micellar structures slightly changed by further addition up to 6 wt%, Table 1. This indicated that the solubilization of 1-pentanol in aqueous phase had reached the limit and the excess of alcohol molecules were most likely solubilized and oriented in the micellar surface, and hydrocarbon core of micelles. However, this alcohol is not enough to affect the micelle hydrophobic core as the length of hydrophobic chain of the alcohol is too short to influence the micellization process.

TABLE 1. Micelle structural parameters from 0.3M SDS solution with addition of n-alcohols. A minor axis, R_a was fixed at 14.3 Å for fitting other SANS experimental data.

[alcohol] wt%	R_b	Axial ratio	α	1st Q_{max} (Å^{-1})	2nd Q_{max} (Å^{-1})	Lamellar Spacing (Å)
0	21.3	1.49	30.5	0.086	-	-
1-Ethanol						
2	19.7	1.38	28.7	0.090	-	-
4	19.2	1.34	26.0	0.092	-	-
6	18.7	1.30	25.3	0.094	-	-
8	17.9	1.25	24.4	0.095	-	-
10	17.2	1.20	23.3	0.097	-	-
1-Propanol						
2	20.1	1.40	29.6	0.090	-	-
4	19.4	1.36	30.8	0.092	-	-
6	18.3	1.28	28.2	0.095	-	-
8	17.8	1.25	26.5	0.098	-	-
10	17.6	1.23	27.3	0.099	-	-
1-Butanol						
2	19.6	1.37	28.0	0.092	-	-
4	18.6	1.30	26.8	0.100	-	-
6	17.9	1.25	26.2	0.104	-	-
8	16.9	1.18	24.4	0.109	-	-
10	16.1	1.13	23.7	0.113	-	-
1-Pentanol						
2	19.8	1.38	26.6	0.096	-	-
4	19.4	1.35	23.6	0.098	-	-
6	18.8	1.31	22.2	0.097	-	-
8	18.4	1.29	19.4	0.096	-	-
10	18.6	1.30	20.5	0.096	-	-
1-Hexanol						
2	22.8	1.60	42.3	0.083	-	-
4	23.0	1.61	29.0	0.079	-	-
6	25.9	1.81	26.6	0.079	-	-
8	-	-	-	0.062	0.168	101
10	-	-	-	0.054	0.114	115
1-Octanol						
2	24.0	1.68	19.9	0.073	-	-
4	25.5	1.78	33.8	0.066	-	-
6	-	-	-	0.042	0.080	145
8	-	-	-	0.039	0.075	160
10	-	-	-	0.044	0.086	140
1-Decanol						
2	29.5	2.06	18.6	0.067	-	-
4	31.4	2.20	16.1	0.060	-	-
6	-	-	-	0.032	0.063	190
8	-	-	-	0.030	0.059	205
10	-	-	-	0.034	0.068	180

It can be verified that solubilized alcohol molecules distribution such as dispersed in the aqueous phase, oriented in the micellar surface, or located in the hydrocarbon core of micelles affected the micellar structure. The different distribution site of alcohol molecules in the 0.3M SDS micellar solution is depending on the hydrophobic chain length alcohol molecule. Short chain alcohol molecules particularly solubilized in the aqueous phase and hydrophilic head group of the micelles as well. This state removed the barriers for structural deformation that decreasing the surface energy at this polar-a polar interface. Medium chain alcohols solubilized in the palisade layer of the micelle and then caused the surfactants molecules more energetically favorable for being a part of micelle. Meanwhile, long chain and more hydrophobic alcohols seem to penetrate deeper into the hydrocarbon interior of micelles and take a part in micellization process.
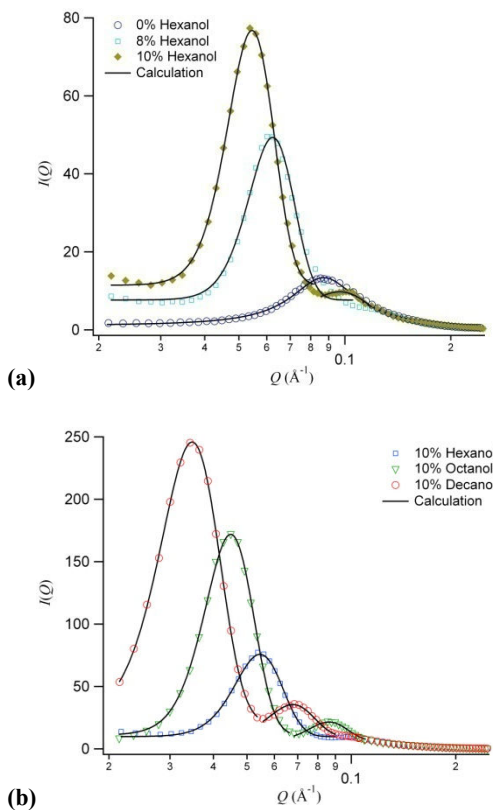

(a)

(b)

FIGURE 4. SANS scattering profiles of 0.3M SDS micellar solution in addition of (a) 1-hexanol at high concentration (d) 10 wt% concentration of 1-hexanol, 1-octanol and 1-decanol.

It is observed from the scattering distribution profile that the addition of 8 wt% *n*-hexanol effectively induces the SDS micellar system into the liquid crystalline phase as the Bragg's peaks of lamellar structure occurred, Figure 4a. Similar fashion also occurs for other micellar systems with longer chain alcohols, i.e. *n*-octanol and *n*-decanol. It is noticeable from Figure 4b that the Bragg's peak significantly shifted from higher Q into lower Q position confirming the lamellar spacing increases from about 100 Å to about 200 Å by increasing the hydrocarbon chain of alcohols at 10 wt% of concentration. It can be described that the micelle hydrophobic core accommodated more alcohol molecules due to decreasing the solubility of alcohol in water and then micelles becomes more ellipsoid (increasing the axial ratio). Once the alcohol reached the critical concentration in the micellar system, the micelles abruptly transform to lamellar structure whereas the alcohol molecules accumulated between two bilayers of SDS micelles.

The structural changes of the SDS micelles by adding the *n*-alcohols correspond to the alteration of the average critical packing parameter ($p = v/(l_c.a_0)$), i.e. the optimum head groups area a_0, the critical chain length l_c, and the hydrocarbon volume v, of the molecules in the micelle [1]. The increasing of the packing parameter due to the increasing of hydrocarbon volume of SDS molecules + long chain alcohol molecules, then the micelle favorably grows to form a longer ellipsoidal shape and lamellar of bilayer structures in further. This phase transition certainly occurred from the experimental results where longer chain alcohol molecules were added into the SDS micellar solution.

CONCLUSION

Analysis of SDS micellar solution using SANS technique has been discussed. The results confirmed the self-assembly mechanism of micelles in the 0.3M SDS micellar solution in addition of *n*-alcohol molecules. Short chain *n*-alcohols entirely dissolved in the aqueous phase and increased the critical micelle concentration by increasing the alcohols concentration. Medium to long chain *n*-alcohols solubilized in the micelle container (micellar phase) that strongly induced the growth of micelles by increasing the length of hydrophobic *n*-alcohols as well as its concentration.

ACKNOWLEDGMENTS

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