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ORIGINAL CONTRIBUTION

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Interactions between anionic mixed micelles and α-cyclodextrin and their inclusion complexes: conductivity, NMR and fluorescence study

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Abstract Mixed micelle formation of anionic surfactants sodium dodecyl sulfate (SDS) and sodium lauroyl sarcosine (SLAS) have been studied in water and in 5, 10, and 15 mM concentrations of α-cyclodextrin (α-CD) over mole fraction range of α_{SDS} from 0 to 1. From the conductivity curves, the critical micellar concentration (CMC) for the pure and binary mixtures were evaluated. The degree of counterion association (χ) or counterion dissociation (δ), the equivalent ionic conductivities of the monomeric species (Λ_{m}), the associated species (Λ_{assc}), and the micelle (Λ_{mic}) were evaluated from the slope of the conductivity vs concentration plots. The CMC values have been used to calculate the thermodynamic parameters such as the standard free energy of micelle formation $\Delta G^{0}_{\mathrm{mic}}$ and a transfer of standard free energy of micelle $\left(\Delta G^{0}_{\mathrm{M,tr}}\right)$ from the aqueous medium to additive medium computed. The apparent CMC of the surfactants varies linearly with α-CD concentrations. From the dependence of CMC of the surfactants on α-CD concentration, we are able to determine the association constant (K) of surfactant-α-CD inclusion complexes assuming 1:1 stoichiometry. Mixed micelle behaves ideally in the pure water as well as at the different concentrations of α-CD, which was evaluated by using the Clint equation, the regular solution approximation, and Motomura's formulation. Self-diffusion coefficients of the micelle increased upon the induction of SDS into the micelle. 2D-rotating frame Overhauser effect spectroscopy spectra of SDS and SLAS were recorded in the presence of α-CD to investigate the interaction between H-atoms of the alkyl chain of the surfactants and H-atoms of the hydrophobic cavity of α-CD indicating multiple complexation. The fluorescence anisotropy of rhodamine B has been measured to observe the structural behavior of mixed micelle.

Keywords Conductivity · SDS · SLAS · CMC · Mixed micelles · α-cyclodextrin · Association constant · NMR · Diffusion coefficient · Fluorescence anisotropy

Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides formed from α-(1→4)-linked D(+)-glucose units [1]. The commercially available α-, β-, and γ-CD, consisting of 6, 7, and 8 glucose units, respectively, are often depicted as hollow truncated cones. The torus structure has a hydrophilic surface which makes CDs water-soluble, whereas the cavity is composed of the glucoside groups, giving a hydrophobic environment. The CDs have been well known to form inclusion complexes with different molecules involving several kinds of driving forces such as Vander

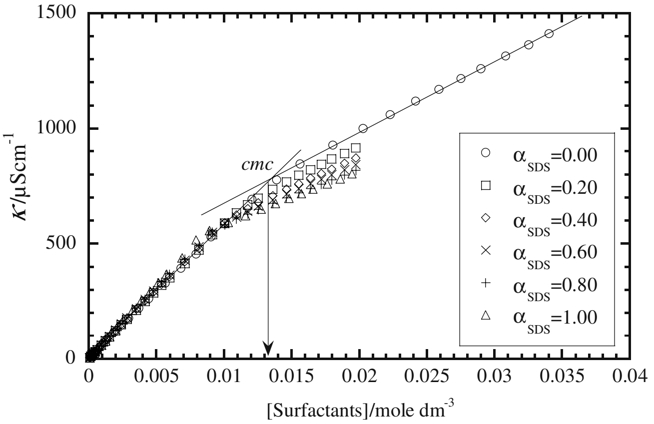


Fig. 1 Plots of κ vs concentrations of pure and binary SDS–SLAS mixture in pure water

Waals and hydrophobic and hydrophilic interactions. The ability of the CD to form inclusion complexes with a wide variety of molecules have led to numerous applications within the pharmaceutical industry as a drug delivery as well as in the food and agrochemical industry [1]. Furthermore, they are often used in studies of molecular interaction in the growing area of supramolecular chemistry. In this work, we have explored the interactions between surfactants surfactants sodium dodecyl sulfate (SDS) and sodium lauroyl sarcosine (SLAS), and the α-CD which consists of six glucose units and is well known to incorporate guest molecules in the hydrophobic cavity predominantly in a 1:1 stoichiometry. The ability of α-CD to complex SDS has been used to study protein refolding and recover protein from otherwise insoluble aggregates [2, 3]. Apart from that, a lot of work has been done to study the inclusion complexes of CDs with different single surfactants system [4–7]. Okubo et al. have studied the 1:1 inclusion complexes of anionic and cationic surfactants with α-, β-, and γ-CD by using conductometric and stopped flow conductivity method and concluded that the association constant significantly depends upon the chain length of detergents and cavity size of the CD, and it is highly influenced by the presence of alcohol [5–7]. Alami et al. have studied interactions of novel non-ionic gemini surfactant with α-, β-, and γ-hydroxylpropyl CDs and observed the structural transition from spherical to rod-shape aggregates by using small angle neutron scattering [8].

Mixed micelles have distinct advantages given by their more favorable properties such as wetting, detergency, and surface-activity as compared to a single surfactant system [9]. Keeping interesting host–guest interactions in mind, we have studied the mixed micelle formation of anionic binary mixtures in the presence of α-CD to observe the changes in the micellar properties. In this work, the surfactants chosen for the binary mixture slightly differ in the alkyl chain lengths and significantly differ in the polarity of the ionic head group, so we expect non-ideal mixing behavior as observed in the case of ionic–nonionic, anionic–cationic, anionic–zwitterionic, and cationic–zwitterionic detergent mixtures due to the existence of favorable interactions [9, 10]. Apart from this, we investigated the formation of complexes between α-CD–SDS and α-CD–SLAS by conductometry and 2D-NMR. From the 2D-NMR rotating frame Overhauser effect spectroscopy (ROESY) intensity data, the solution structures of these complexes were estimated and indicate that the formation of multitude inclusion complex structures or multiple complexation or both exist in the bulk solution.

Experimental

The SDS and SLAS from Sigma, both surfactants more than 99% pure, were used as received. α-CD (Cavamax W6, pharmaceutical grade) from Wacker Chemie GMBH, Burghausen, Germany was used as received. All solutions were prepared in Milli-Q water.

Methods

The specific conductances of pure and binary mixtures of SDS and SLAS in pure water and in different concentrations of α-CD were obtained by using a digital conductivity bridge (Model CDM-210, Meter Lab, Radiometer, Copenhagen, Denmark) attached with a dip-type conductivity cell with double-walled jacket in which thermostated water was circulated. The capacity of the conductivity cell was 150 cm^3. Before starting the experiment, the system was equilibrated at 25°C for at least 30 min. An automatic thermostated bath from Lauda Model RE 104, Germany was used for maintaining the temperature within ±0.1°C. The cell constant of the conductivity cell was 1.691 cm^{-1}, which was determined by using a KCl solution of known conductivity as reference.

All the fluorescence anisotropy measurements were performed on a Perkin Elmer LS-55 spectrometer (Perkin–Elmer, England) at 25±0.1°C. This apparatus is equipped with a 150-W xenon lamp as the excitation source and a thermostated cell housing chamber which is fitted with a circulating water bath to control the temperature. Rhodamine B (RB) was used as a fluorescence probe. Fluorescence anisotropies were measured by using excitation and emission wavelengths of 557 and 576 nm, respectively. The size of both emission and excitation slits were kept at 10 nm. For all the measurements, a 10-mm quartz cell was used. The concentration of RB was kept at 1 μM.

Fluorescence anisotropies were measured in the same apparatus equipped with a polarization accessory, which uses the L-format instrumental configuration and an automatic interchangeable wheel with polarizers. The fluorescence anisotropies were determined as follows:

$$r = \frac{I_V - G_H}{I_V + 2GI_H} \tag{1}$$

where the subscripts of the fluorescence intensity values (*I*) refer to the vertical (V) and horizontal (H) polarizer orientation. The instrument is equipped with software which is able to determine the instrumental configuration factor *G* required for the L-format configuration. The anisotropies were averaged over an integration time of 10 s. A minimum of four readings were taken individually for each sample. The anisotropy values of the probe RB in micelle medium are taken as the average value of four measurements.

All NMR measurements were conducted on a BRUKER DRX-600 spectrometer operating at field strength of 14.1 T, equipped with a triple-gradient TXI (H/C/N) probe. The self-diffusion coefficients were measured at 19° C to minimize convective flow and by using the double-stimulated echo pulse sequence [11]. Each experiment was recorded with varying the gradient strength from 0.3 to 40 Gcm^{-1} in 32 steps. The applied gradient pulses were sinusoidal. Diffusion constants were obtained from integrating the $OSO_2O\text{-}CH_2$ and $N\text{-}CH_3$ signals, respectively, in the double-stimulated echo diffusion experiment and subsequent fitting of the integrals vs the gradient strength to the following Stejskal–Tanner equation [12]:

$$I = I_0{}^{*}e^{-\left(\Delta-\frac{\tau}{3}\right)\gamma^2 G^2 \tau^2 D} \tag{2}$$

where *I* is the observed echo intensity, I_0 is the echo intensity in the absence of field gradient pulses, γ is the gyromagnetic ratio, *G* is the field gradient strength, τ is the duration of the gradient pulse, and Δ is the time between the leading edges of the gradient pulses. Diffusion coefficients of the monomeric surfactant molecules were measured at a concentration of 1/3 of their critical micellar concentration (CMC). Diffusion coefficients of the micelles were measured in solutions containing a total of 140 mM surfactant in varying compositions for both surfactants.

The 2D ROESY spectra with a 150-ms spin lock of 1.7 kHz were recorded at 25°C of samples containing 10 mM α-CD and 10 mM SDS or 18 mM SLAS. The residual solvent signal was suppressed by presaturation. CD resonances were assigned by the help of a gradient selected 2QF-COSY spectrum with presaturation.

Results and discussions

Conductivity behavior

Figure 1 shows the experimental values of specific conductance, κ, vs concentration of pure and binary SDS–SLAS mixture of surfactant in water. Each plot shows the single break point indicating the pure and mixed micellization of surfactants. From the break point, the CMC is evaluated by fitting the premicellar and post-micellar region into linear regression analysis giving correlation factors 0.9990 to 0.9995. The intersection point between the two straight lines gives the CMC value. Similar plots were obtained for the pure and binary mixture of surfactants in the presence of α-CD (data not shown). The CMC values obtained from κ measurements for pure and binary mixture of surfactants with and without α-CD are listed in Table 1. The CMC values obtained for pure surfactants closely agree with the literature values [9].

To understand the κ behavior over the whole mole fraction range, we have computed the equivalent con-

Table 1 Values of critical micellar concentration, CMC/10^{-3} mol dm^{-3} for the pure SDS, SLAS, and SLAS, SDS mixtures in pure water and in different α-CD concentrations at 25±0.1°C

Water	
α_{SDS}	CMC (mM)
0.00	13.90
0.20	11.80
0.40	10.51
0.60	9.84
0.80	9.31
1.00	8.50
5 mM α-CD	
0.00	18.00
0.20	15.64
0.40	14.13
0.60	13.16
0.80	12.12
1.00	11.80
10 mM α-CD	
0.00	21.90
0.20	18.50
0.40	17.30
0.60	16.43
0.80	14.76
1.00	13.50
15 mM α-CD	
0.00	25.50
0.20	22.50
0.40	20.10
0.60	18.40
0.80	17.40
1.00	16.40

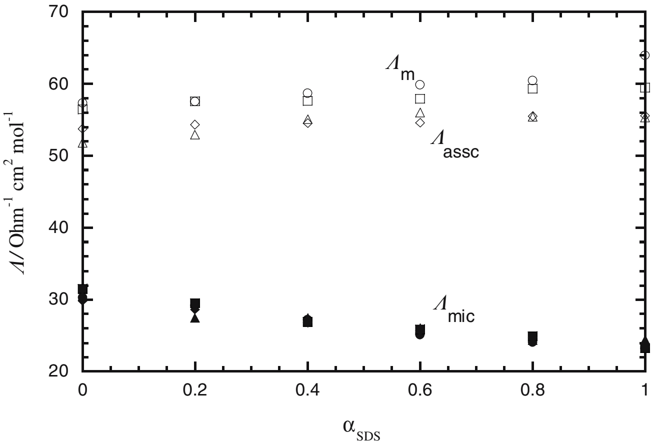


Fig. 2 Plot of Λ_m, Λ_{assc}, and Λ_{mic} vs α_{SDS} for SDS and SLAS binary mixture in pure water and in different concentrations of α-CD. *Open and filled circles* represent Λ_m and Λ_{mic} in pure water, respectively. *Open squares*, *open diamonds*, and *open triangles* represent Λ_{assc} in 5, 10, and 15 mM α-CD. *Filled squares*, *filled diamonds*, and *filled triangles* represent Λ_{mic} in 5, 10, and 15 mM α-CD

ductances of monomer (Λ_m), associated (Λ_{assc}), and the micelle (Λ_{mic}) states of surfactant electrolytes from the slope of the κ plots in the premicellar as well as postmicellar regions. In the presence of water, the conductivity of monomeric species (Λ_m) can be calculated through the slope of the premicellar region. Similarly, Λ_{assc} can also be obtained in the presence of α-CD. Λ_{assc} describes the effective conductivity of a mixture of monomer and monomer complexes. On the other hand, the conductivity of the monomers remains almost constant after the CMC, therefore, Λ_{mic} can be calculated from the slope of κ in the postmicellar region in the absence and in the presence of α-CD. The Λ values so obtained for pure and binary mixture in pure water and different concentrations of α-CD are shown in Fig. 2. If we compare the value of Λ_m in water of SDS and SLAS, it shows that Λ_m for SLAS is lying lower than those of SDS probably due to the presence of bulky polar head group which reduces the mobility of ionic species in the bulk phase, whereas values for the binary mixture increase more or less in a linear fashion. The reported value of Λ_m of SDS is in close agreement with the literature value [5]. The obtained Λ_{mic} for SDS is 23 Ω^{-1} cm^2 mol^{-1} which is close to the value 22 Ω^{-1} cm^2 mol^{-1}obtained by Okubo et.al, whereas Λ_{assc} value reported in this work for SDS, α-CD, and water is 55–59 Ω^{-1} cm^2 mol^{-1} in 5–15 mM α-CD range, which is slightly higher than the 44 Ω^{-1} cm^2 mol^{-1} reported for the same system by Okubo et al. in the present 11–45 mM concentration range of α-CD [5].

A comparison between Λ_m and Λ_{assc} shows that Λ_m is larger than Λ_{assc} for the present binary mixture on the entire mole fraction range in the submicellar region. The decrease of Λ_{assc} with increasing CD concentration clearly demonstrates the incorporation of surfactant monomer into the CD cavity, because incorporation of the surfactant in to the cavity will partly shield the charge of the ionic polar group and thus reduce conductance. This value further decreased slightly with the increase of CD concentration which shows that more surfactant monomers incorporate the CD cavity. On the other hand, the values for Λ_{mic} were not much affected in the presence of α-CD (Fig. 2).

Degree of counterion association (χ) or dissociation (δ)

In the literature, several methods exist to evaluate the value of degree of counterion dissociation, δ, with the widely used is that which estimates δ from the ratio of the slopes above (S_2) and below (S_1) the CMC in the κ vs C of surfactant plots. Subsequently, the degree of counterion associated χ, i.e., χ=(1−δ) can be computed and shown in Fig. 3 [13]. The χ value for SDS agreed well with the literature value [14]. The evaluated χ for SLAS is lower than that of SDS. This result indicates that steric head group incompatibility of the polar head group of SLAS reduces the adsorption of the counterion at the micelle surface and leads to formation of the loose bulky micelle as compared to the compact micelle of SDS. The χ increases linearly with the increase in the amount of SDS, indicating stabilization and formation of compact micelles with a high degree of counterion association. Furthermore, the χ values in α-CD are lower than those in pure water and further decrease with the increase in the concentration of α-CD.

Relation between CMC, α-CD, and association constant (K)

To see the effect of α-CD on the micellization process, we have carried out conductivity experiments to evaluate the

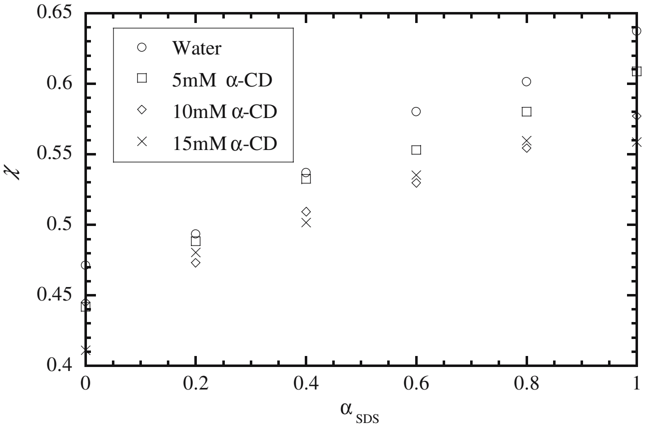


Fig. 3 Plot of degree of counterion association, χ, vs α_{SDS} for SDS and SLAS binary mixture in pure water and in different concentrations of α-CD

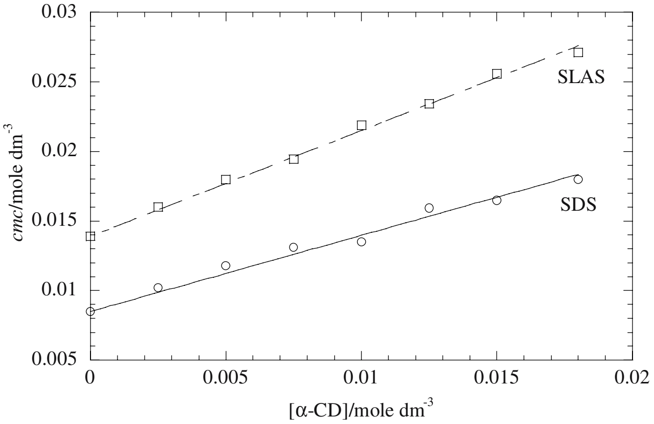


Fig. 4 Plot of CMCs of SDS and SLAS vs concentrations of α-CD

CMC value of SDS and SLAS at different concentrations of α-CD. As shown in the Fig. 4, the apparent CMC values of SDS and SLAS are linearly correlated with the α-CD concentration which indicates that more surfactant monomers form inclusion complexes with α-CD and lead to a delay in the micelle formation. From these data, we are able to evaluate association constant (K) between surfactant and α-CD in the submicellar concentration by assuming a 1:1 association stoichiometry as given by:

$$\mathrm{CD}+S \leftrightarrow \mathrm{CD}:S \tag{3}$$

$$\mathrm{K} = [\mathrm{CD}:S]\,/\,[\mathrm{CD}]\ [S] \tag{4}$$

$$[\mathrm{CD}]_\mathrm{t}=[\mathrm{CD}]+[\mathrm{CD}:S] \tag{5}$$

$$[\mathrm{CD}]=[\mathrm{CD}]_\mathrm{t}/1+K[S] \tag{6}$$

$$[S]_\mathrm{t}=[S]+[\mathrm{CD}:S] \tag{7}$$

By substituting Eq. 4 into 7, we get

$$[S]_\mathrm{t}=[S]+K[\mathrm{CD}][S] \tag{8}$$

By substituting Eq. 6 into 8, we get

$$[S]_\mathrm{t} = [S] + K[S][\mathrm{CD}]_\mathrm{t}/1 + K[S] \tag{9}$$

Where K, CD, S, CDS, $\mathrm{CD_t}$, and S_t are the association constant, free CD, free surfactant, inclusion complex, total CD, and total surfactant concentrations at CMC, respectively. Equation 9 predicts a linear correlation between S_t and $\mathrm{CD_t}$ which we also observe in Fig. 4. This leads to association constants of α-CD–SDS and α-CD–SLAS of 142 M^{-1}±8 and 229 M^{-1}±12, respectively, indicating that SLAS binds more strongly with α-CD than SDS. A detailed overview of binding constant evaluation is given in reference [15]. The present K value for α-CD–SDS is in close agreement with 160 and 110 M^{-1} evaluated by kinetic and conductometric methods, respectively [5, 6]. From the literature review, K values obtained for α-CD–SDS are 1,120, 21,000, and 754 M^{-1} which clearly indicate that the association constant between host–guest molecules significantly depends upon the technique used for their evaluation [16–18]. On the other hand, different techniques such as conductivity, electrochemical, surface tension, NMR, calorimetry, and UV–Visible spectroscopy have been used to estimate the association constant of CDs with various guest molecules [5–7]. UV–Visible spectroscopy has been applied to determine association constants of CD inclusion complexes by monitoring the changes in the absorbance of species in the UV region. Therefore, it is impossible to determine association constant if the species do not possess chromophoric group using this method [5, 19–21]. Recently, Funasaki et al. determined the 1:1 and 1:2 complexes formation between cationic surfactant dodecyltrimethylammonium bromide and α-CD through chemical shift data of protons by using one- and two-dimensional proton NMR spectroscopy [7].

Mixed micelle formation in pure water and in α-CD

To explore surfactants–α-CD interactions in detail, we have evaluated the CMC of pure SDS, SLAS, and their binary mixtures in water and in different concentrations of CD. The CMC values are listed in Table 1 and graphically shown in Fig. 5. The CMC values in the presence of α-CD

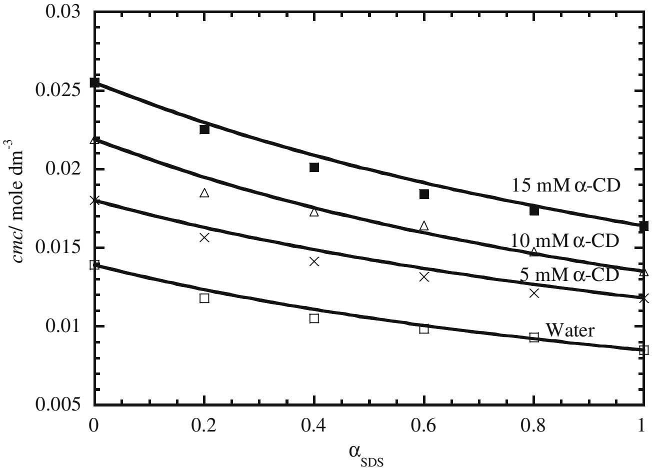


Fig. 5 Plot of mixed CMC vs α_{SDS} for SDS and SLAS in pure water and in different concentrations of α-CD. Predicted CMC* (*line*), experimental CMC (data points)

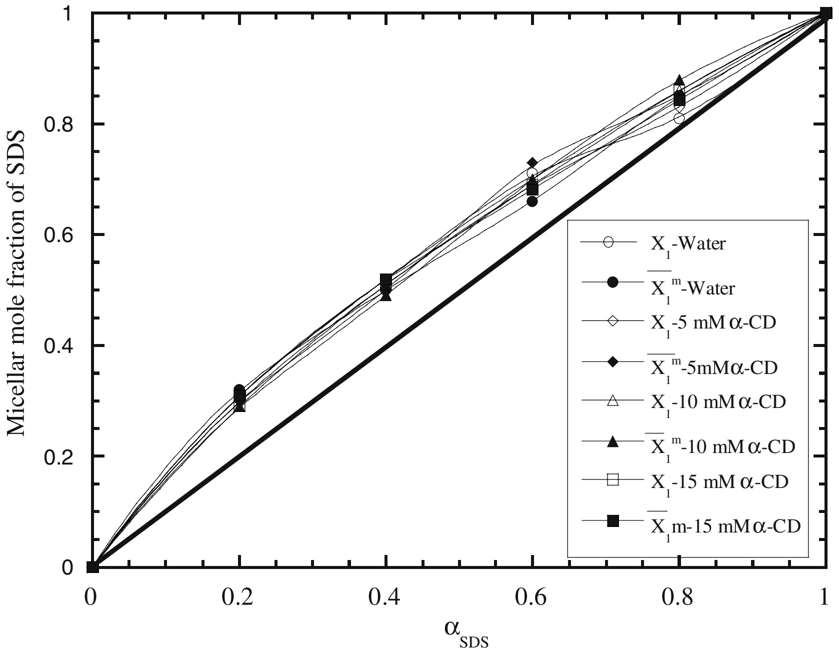


Fig. 6 Plot of mole fraction of SDS in the mixed micelle (x_1) vs mole fraction in the bulk (α) for SDS and SLAS mixtures in pure water and in different concentrations of α- CD. *Open marker* indicates x_1 obtained from regular solution approximation, whereas *closed marker* indicates x_1 obtained from Motomura's formulation. *Solid line* predicts the ideal value, and experimental values are shown as data points

are higher than in water system, and these values further increase with the increase in the concentration of α-CD, indicating that more surfactant molecules are required to form inclusion complexes with the CD at high concentration. It is also possible to evaluate the ideality or non-ideality of mixed micelles of SDS and SLAS in water as well as in the presence of CD by using pseudo phase thermodynamic model to obtain quantitative information [22]. This model relates the ideal mixed CMC* with the experimental CMC of the pure components by using the following equations:

$$C_1 = x_1 \mathrm{CMC}_1 = \alpha_1 \mathrm{CMC}^* \tag{10}$$

and

$$C_2 = (1 - x_1)\mathrm{CMC}_2 = (1 - \alpha_1)\mathrm{CMC}^* \tag{11}$$

Equation 12 can be obtained after combining Eqs. 10 and 11

$$\frac{1}{\mathrm{CMC}^*} = \frac{\alpha_1}{\mathrm{CMC}_1} + \frac{(1 - \alpha_1)}{\mathrm{CMC}_2} \tag{12}$$

The α_1 and x_1 are the mole fractions of surfactant 1 (SDS) in the total mixed solute and in the mixed micelle, respectively. The CMC_1, CMC_2, C_1, and C_2 are the critical micellar concentrations and the overall concentrations in the micelle formation of components 1 and 2, respectively. The experimental CMC values lie close to an ideal CMC* at whole mixing range indicating that the mixed micelle formation is essentially ideal in nature in water as well as in the presence of α-CD (Fig. 5). These results have been further confirmed by using the regular solution approximation [23]. The x_1 can be iteratively computed from the following equation:

$$\frac{x_1^2 \ln\left(\mathrm{CMC}\alpha_1/\mathrm{CMC}_1 x_1\right)}{(1 - x_1)^2 \ln\left[cmc(1 - \alpha_1)/\mathrm{CMC}_2(1 - x_1)\right]} = 1 \tag{13}$$

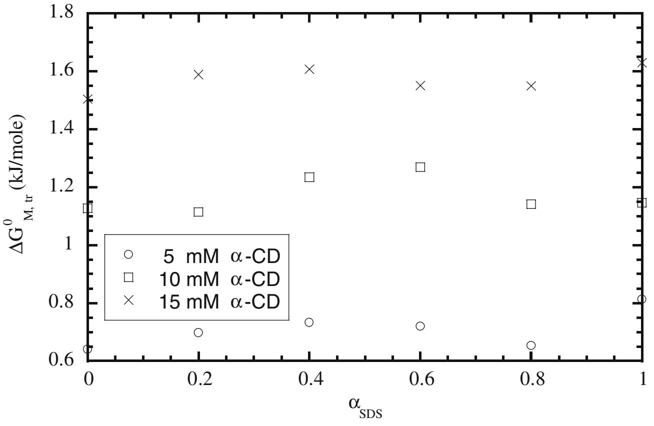


Fig. 7 Plot of $\Delta G^{o}_{M,tr}$ vs α_{SDS} for SDS and SLAS in pure water and in different concentrations of α-CD

Table 2 Values of experimental determined diffusion coefficient, D_{obs}, micellar fraction of SDS in the micelles, X_{SDS}, and diffusion coefficient of the micelles, D_{mic}, for the pure and SDS and SLAS mixtures from NMR measurements

α_{SDS}	$D_{obs,SDS}$ (10^{-11} m^2 s^{-1})	$D_{obs,SLAS}$ (10^{-11} m^2 s^{-1})	X_{SDS}	D_{mic} (10^{-11} m^2 s^{-1})
0.00	–	6.92±0.06	0.00	2.99
0.20	6.22±0.04	6.68±0.05	0.20	3.59
0.40	6.25±0.04	6.44±0.05	0.40	3.47
0.60	6.26±0.04	6.45±0.05	0.60	3.53
0.80	6.30±0.05	6.22±0.05	0.80	3.65
1.00	6.36±0.04	–	1.00	3.65

The observed diffusion coefficients are given together with the uncertainty obtained from the fitting routine. The uncertainty of the micellar diffusion coefficients was estimated from varying the D_{obs} values within their error limits (±2%) and proved to be of the same order than the uncertainty in the D_{obs} values

These values are graphically shown in Fig. 6. From the x_1 values, the interaction parameter, β, can be computed by the following equation:

$$\beta = \ln\left(\frac{\mathrm{CMC}\alpha_1}{\mathrm{CMC}_1 x_1}\right) \Big/ (1 - x_1)^2 \qquad (14)$$

The β value demonstrates the extent of interaction between the two surfactants which lead to the deviation from ideal behavior. Negative and positive β values suggest attractive and repulsive interactions between two surfactants in the mixed micelle, respectively. For the ideal mixing of no interaction, the β value should be close to 0. The average β values computed for the present binary mixtures are −0.07, −0.3, −0.2, and −0.3 in pure water, 5, 10, and 15 mM α-CD, respectively. These values do not represent significant changes even in the presence of CDs and more or less close to 0 indicating that mixed micelle formation is close to ideal in nature. From the present mixed CMC data, it is also possible to compute CD contribution in the mixed micellization process (ΔCMC) by subtracting the CMC of the surfactant in pure water from the CMC value in the presence of additive (i.e., CMC at each mole fraction in the different CD concentrations) by using Fig. 5 and Table 1. The ΔCMC values do not show much change at the 5, 10, and 15 mM CD over the whole mole fraction range of SDS indicating an equal effect of CD at whole mole fraction range.

We have evaluated the standard free energy of micellization from the CMC data $\left(\Delta G^{o}_{mic}\right)_{W} = RT \ln X_{CMC}$. These values are negative, demonstrating the spontaneity of mixed micelle formation. However, these values decrease in the presence of CD indicating that micelle formation becomes less favorable (data not shown). It is also possible to evaluate the effect of additive on micellization by means of standard free energy of transfer micelle from aqueous phase to aqueous additive $\left[\Delta G^{o}_{M,tr} = \left(\Delta G^{o}_{mic}\right)_{CD+W} - \left(\Delta G^{o}_{mic}\right)_{W}\right]$. These values are positive at entire SDS mole fraction range at different CD concentrations (Fig. 7), demonstrating that the presence of CD additive makes the micelle formation unfavorable. Moreover, these values increase with the increase of CD additive concentration, indicating to delay the mixed micelle formation.

To check the present results obtained from pseudo phase thermodynamic model and regular solution approximation, the equation of Motomura et al. [24], based on excess thermodynamic quantities, was applied. The mixed micelle composition can be determined by using following the equation:

$$\bar{x}_2^m = \bar{x}_2 - \left(\bar{x}_1 \alpha_2 / \overline{\mathrm{CMC}}\right)\left(\partial \overline{\mathrm{CMC}} / \partial \bar{x}_2\right)_{T,P} \qquad (15)$$

and

$$\overline{\mathrm{CMC}} = (v_1 x_1 + v_2 x_2)\mathrm{CMC} \qquad (16)$$

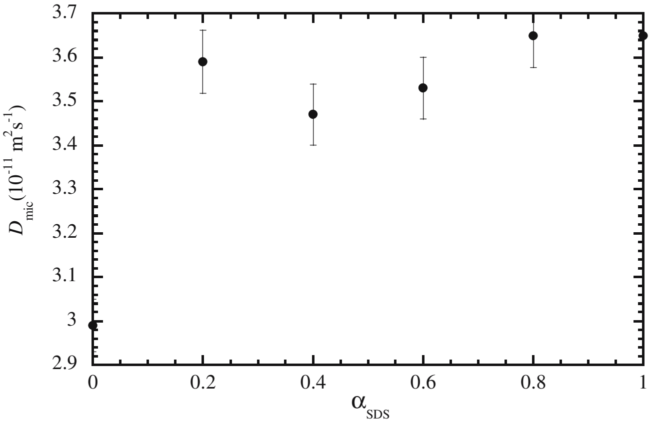
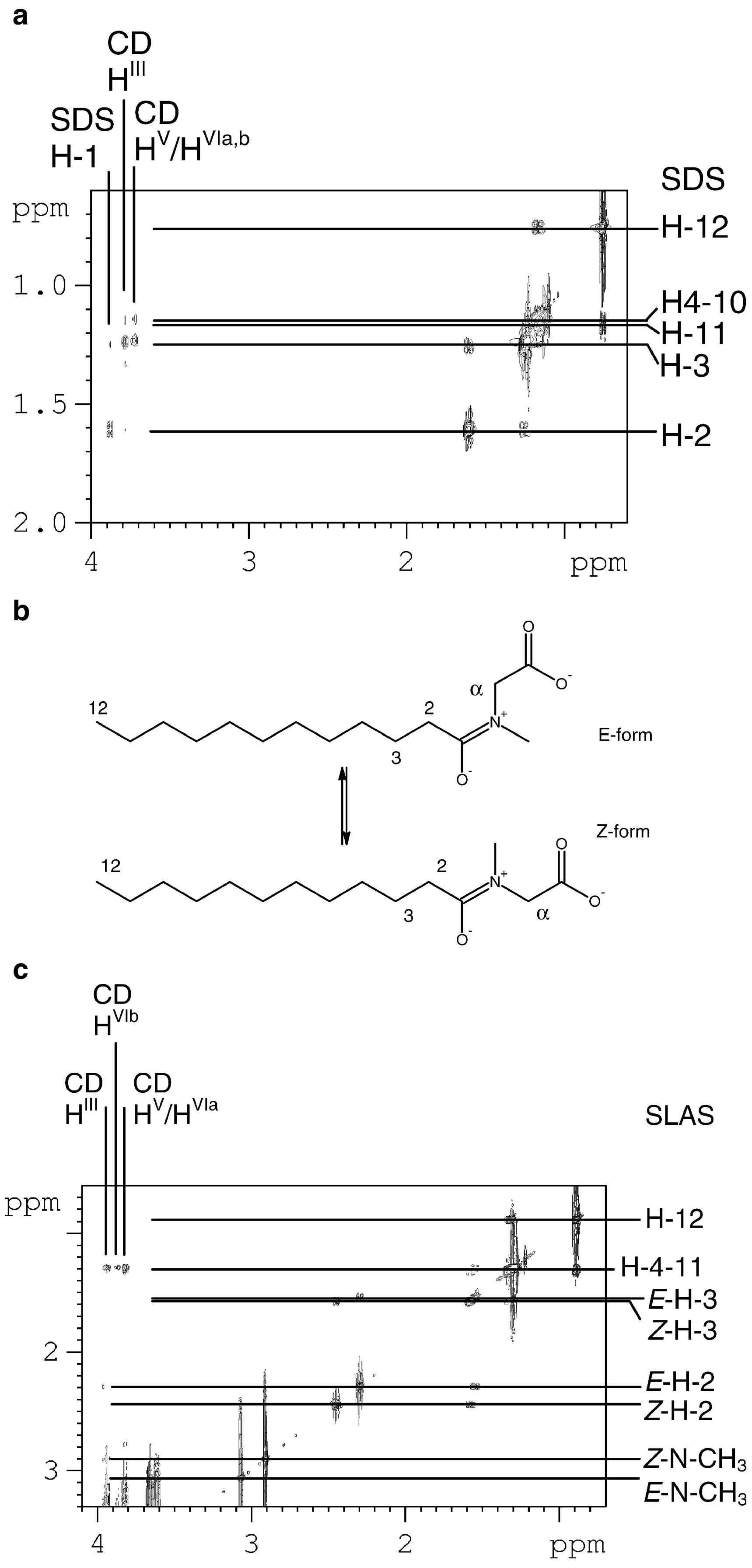


Fig. 8 Plot of D_{mic} vs α_{SDS} for SDS and SLAS in pure water

Fig. 9 **a** Area of 2D-ROESY NMR spectra of a solution containing SDS and α-CD. Positions of cyclodextrin signals (*Roman numerals*) and SDS signals (*Arabic numerals*) are indicated. **b** Structural representation of Cis (*Z*) and Trans (*E*) isomers of SLAS. **c** Area of 2D-ROESY NMR spectra of a solution containing SLAS–α-CD. Positions of cyclodextrin signals (*Roman numerals*) and SLAS signals (*Arabic numerals*) are indicated



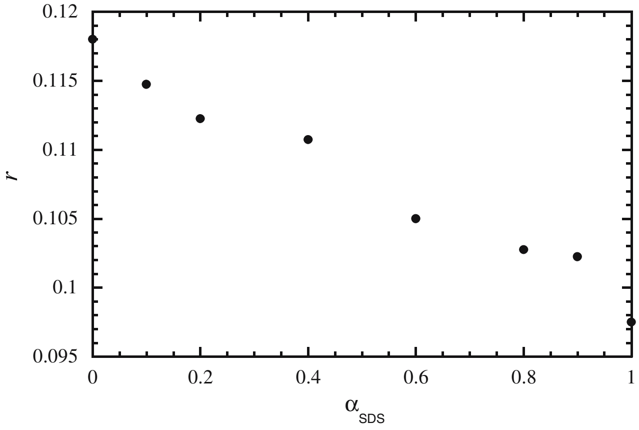


Fig. 10 Plot of fluorescence anisotropy (r) vs α_{SDS} for SDS and SLAS in pure water

where $\bar{x}_2^m$ and $\bar{x}_2$ are the mole fractions in the micelle and in the bulk phase of component 2 (SLAS), respectively. $\bar{x}_2$ is given by

$$\bar{x}_2 = v_2\alpha_2 / (v_1\alpha_1 + v_2\alpha_2) \tag{17}$$

where v_1 and v_2 are the numbers of ions produced by the surfactant upon dissociation. Similarly, $\bar{x}_1^m$ is evaluated for component 1 (SDS). The x_1 (regular solution approximation) and $\bar{x}_1^m$ (Motomura's formulation) values are computed from κ measurements and plotted in the Fig. 6, which reveals the composition of the surfactant in the mixed micelle and in the bulk mole fraction (α_1). The x_1 and $\bar{x}_1^m$ deviate positively from ideality, indicating that mixed micelles are rich in SDS in water as well as in the presence of CD. It is clear that the presence of CD does not influence the micelle composition. We noted the good reproducibility in the values of micellar composition obtained from different methods.

NMR measurements

It is well known that there are two processes occurring in the surfactant solution above the CMC. The first is the rapid exchange of surfactant molecules of the micelle with the surfactant molecules present in the bulk solution, and the second is the disintegration and reforming of micelles itself, which is a slow process. The latter process is correlated with the average lifetime and stability of the micelle. The monomer lifetime in the micelle is small on the timescale of pulsed gradient spin echo experiments, so all self-diffusion coefficients will become time-averaged. Therefore, the observed diffusion coefficient, D_{obs}, can be expressed as the population-weighted average of the high self-diffusion coefficient of the monomers, D_{mon}, and smaller self-diffusion coefficient of the micelles, D_{mic} [25]. The diffusion coefficients obtained from micellar solutions are a weighted average from the monomeric and the micellar-bound molecules [26]:

$$D_{\mathrm{obs}}^{\mathrm{i}} = p_{\mathrm{i}} D_{\mathrm{monomer}}^{\mathrm{i}} + (1 - p_{\mathrm{i}}) D_{\mathrm{mic}} \tag{18}$$

where p_i denotes the fraction of monomeric surfactant (i) molecules. Assuming that the monomer concentration of the surfactant always is equal to its concentration at the CMC, p_{i} is given by:

$$p_{\mathrm{i}} = \mathrm{CMC}_{\mathrm{i}}^{*} / c_{\mathrm{i}} \tag{19}$$

where c_{i} is the total concentration of surfactant i and $\mathrm{CMC}_{\mathrm{i}}$* denotes the CMC of surfactant i in the mixture. $\mathrm{CMC}_{\mathrm{i}}$* is given by:

$$\mathrm{CMC}_{\mathrm{i}}^{*} = c_{\mathrm{i}} - x_{\mathrm{i}}(c_{\mathrm{t}} - \mathrm{CMC}^{*}) \tag{20}$$

where x_{i} is the mole fraction of surfactant i in the micelles, c_{t} is the total concentration of surfactants $\left(\sum_{\mathrm{i}} c_{\mathrm{i}}\right)$, and CMC* is the CMC of the mixture. In the case of the pure compounds, p can be calculated as CMC/c, where c is the total surfactant concentration. These equations can then be combined to obtain D_{mic} as shown in Eq. 21. Because c_{t} and c_{i} are known, and CMC* was obtained from other measurements, the only remaining variable was x_{i}. The x_{i} and D_{mic} could be obtained simultaneously by looking for the value of x, where the micellar diffusion coefficient of SLAS and SDS are equal. Because they are in mixed micelles, their micellar diffusion coefficient has to be equal.

$$D_{mic} = \frac{D_{\mathrm{obs}}^{\mathrm{A}} - \frac{c_{\mathrm{A}} - x_{\mathrm{A}}(c_{\mathrm{t}} - \mathrm{CMC}^{*})}{c_{\mathrm{A}}} D_{\mathrm{monomer}}^{\mathrm{A}}}{1 - \frac{c_{\mathrm{A}} - x_{\mathrm{A}}(c_{\mathrm{t}} - \mathrm{CMC}^{*})}{c_{\mathrm{A}}}} = \frac{D_{\mathrm{obs}}^{B} - \frac{c_{\mathrm{B}} - (1 - x_{\mathrm{A}})(c_{\mathrm{t}} - \mathrm{CMC}^{*})}{c_{B}} D_{\mathrm{monomer}}^{\mathrm{B}}}{1 - \frac{c_{\mathrm{B}} - (1 - x_{\mathrm{A}})(c_{\mathrm{t}} - \mathrm{CMC}^{*})}{c_{\mathrm{B}}}} = D_{mic} \tag{21}$$

The subscripts and superscripts A and B denote the components A (SDS) and B (SLAS), respectively. The D_{mic} values were computed and mentioned in the Table 2 and shown in Fig. 8. The values for D_{mon} of SDS and SLAS are 4.83×10^{-10} and 4.26×10^{-10} m^2/s, respectively. This agrees well with the observation that Λ_{m} of SLAS is slightly smaller than Λ_{m} of SDS. However, the micellar diffusion constant D_{mic} for pure SLAS micelles is slightly lower than for pure SDS micelles. D_{mic} jumps to a higher value already at 0.2 mol fraction of SDS, after which it remains constant. This can be rationalized in two ways. Firstly, and most simply, the SLAS could be larger resulting in slow mobility compared to the more compact SDS micelles with high degree of mobility. Secondly, the glycine-derivative SLAS could lead to a more viscous medium, which becomes less viscous upon introduction of SDS. This result matches exactly with the micellar composition obtained from different theories. The decrease in D_{mic} of Tween-20 in the glycol viscous medium is reported by Ruiz et al. [27].

Structure of inclusion complex with α-CD

SDS–α-CD complexation

For CD, the signals of H^{V}, H^{VIa} and H^{VIb} over overlapped, so cross peaks to these atoms could not be distinguished from one another. For SDS, only H-1, H-2, and H-12 gave well-separated signals; the remaining CH_2 groups overlapped and could not be distinguished. The ROESY spectrum shows interactions between H^{III} and $H^{V/VI}$ to all SDS signals except for H-1 as shown in Fig. 9a. The interactions with H-12 are very weak. This is indicative of the alkyl chain of SDS being situated in the hydrophobic cavity of α-CD. Because the whole chain is too long to be included in one CD molecule at once, the presence of cross peaks between H^{III} and $H^{V/VI}$ and the whole SDS chain indicates that there is either a multitude of inclusion complex structures or multiple complexation or both.

SLAS–α-CD complexation

Due to the partial double bond character of an amide bond, SLAS exists in two isomers, a *Z*- and an *E*-form, as shown in Fig. 9b. These two forms are at equilibrium, exchanging slowly on the NMR timescale under our measurement conditions. Thus, both the N-CH_3 and the α-CH_2, 2-CH_2, and 3-CH_2 group signals were split into two signals. The signals of the *E*-form could be assigned based on a strong ROESY cross peak between the α-CH_2 and the 2-CH_2, which can only be expected to occur in the *E*-form. Signal integration yielded an equilibrium composition of 54% *E*-form and 46% *Z*-form. Due to signal overlap, the signals of the CH_2 groups 4–11 of SLAS could not be distinguished. Likewise, the signals of H^{V} and H^{VIa} of α-CD were overlapping, whereas the signal of H^{VIb} had its unique chemical shift as shown in Fig. 9c. In addition, α-CH_2 group of SLAS is very closely situated to the H^{III} from α-CD. ROESY cross peaks could be seen from H^{III}, $H^{V/VIa}$, and H^{VIb} signals to all CH_2 groups in the lauryl chain. As is the case with SDS, the whole alkyl chain is in contact with the hydrophobic cavity of the CD molecule, indicating either a fast-interchanging multitude of complex structures or multiple complexation or a combination thereof.

Fluorescence anisotropy

To study the mixing behavior of two unlike components in the mixed micelle, we have performed the polarized fluorescence measurements by using RB as fluorescence probe. The behavior of this probe in micellar medium is well characterized by Jobe and Verral [28]. The degree of depolarization of the fluorescence emission of a probe is measured of its rotational diffusion during the excited lifetime. The fluorescence anisotropy (*r*) is related to the viscous medium around the probe by Perrin's equation as follows:

$$\frac{r_0}{r} = 1 + \frac{kT\tau}{V\eta} \tag{22}$$

where r_0 is the limiting value of emission anisotropy obtained in the absence of rotational freedom, k is the Boltzmann constant, T is the temperature, τ is the average lifetime of the fluorophore excited state, V is the effective molecular volume of the probe, and η is the viscosity around the probe. From Eq. 22, it is clear that a higher or lower r value corresponds to a more rigid and fluid environment, respectively. The values of fluorescence anisotropies are shown in the Fig. 10. Some interesting points can be drawn from Fig. 10. First of all, the r value of RB in pure SLAS micelle is higher than those in pure SDS micelle, clearly revealing the more rigid, less mobile or viscous environment of SLAS. This result directly corresponds to low D_{mic} value of SLAS in comparison to SDS. For the binary mixture, r value decreases in a linear fashion with increasing SDS concentration. This suggests that the penetration of SDS induced a less rigid and viscous environment around the probe in the micelle. This result directly corresponds to the high micelle composition of SDS in the mixed micelle as described in the previous section. Similar trends of decrease in r value for RB and diphenylbutadiene (DPB) were observed for the binary mixture of nonionic–anionic and for DPB in the case of nonionic–cationic surfactant mixture [29, 30].

Conclusion

The physicochemical properties of mixed micelle of SLAS and SDS have been studied in aqueous and at different concentrations of aqueous α-CD by using κ, NMR, and fluorescence measurements. The formation of inclusion complex remarkably changes the micellar properties of pure and mixed micelle. Mixed micelle formation in the presence of α-CD is close to ideal in nature. The increase in

D_{mic} and decrease in *r* value upon the induction of SDS into the mixed micelle indicate the compact, more mobile and less rigid environment of the micelle, respectively. From 2D-ROESY measurements, it can be concluded that both surfactants form either a multitude of inclusion complex structures or multiple complexation or both.

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