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# Self-assembly of sodium bis(2-ethylhexyl) sulfosuccinate in aqueous solutions: Modulation of micelle structure and interactions by cyclodextrins investigated by small-angle neutron scattering

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## ABSTRACT

The modulating effects of  $\alpha$ -cyclodextrin ( $\alpha$ -CD) and hydroxypropyl  $\beta$ -cyclodextrin (HP- $\beta$ -CD) on micelles formed in water by the double tail surfactant sodium bis(2-ethylhexyl) sulfosuccinate (also known as dioctyl sulfosuccinate (DOSS) or Aerosol-OT (AOT)) have been investigated using small angle neutron scattering (SANS). SANS data were fitted to the core-shell oblate ellipsoid form factor and Hansen-Hayter-based structure factor in order to quantify the effect of cyclodextrins on the micelle structure and inter-micelle interactions. The results suggested that addition of cyclodextrins caused a sharp decrease in surfactant aggregation numbers, micelle dimensions and micelle charge. The micelle shape changed from elongated oblate to sphere upon addition of cyclodextrin at stoichiometric ratio of 1:1 CD:AOT for HP- $\beta$ -CD and 2:1 for  $\alpha$ -CD. HP- $\beta$ -CD was found more effective than  $\alpha$ -CD in influencing the micelle properties. For example, the decrease in surfactant aggregation number upon addition of 1 mM CD at constant total surfactant concentration was about double for HP- $\beta$ -CD compared to  $\alpha$ -CD. The results are consistent with the localization of small amount of cyclodextrins in the micelle, while the remainder stays in the solution pseudophase. The present study offers an improved understanding on the modulating effects of CDs on micelle structure and enables better design of emulsifiers or dispersants in formulations suitable for controlled release of actives.

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## 1. Introduction

Sodium bis(2-ethylhexyl) sulfosuccinate, also known as dioctyl sulfosuccinate (DOSS) or Aerosol-OT (AOT), is an anionic double-tail surfactant with relatively low solubility in water but high solubility in oil [1,2]. Because of its remarkable interfacial properties, AOT has been widely used as a stabilizer for microemulsions without the need of co-surfactant [3–7]. Due to its relatively low toxicity and high versatility, AOT finds applications as petroleum dispersant [8–10], as adjuvant or wetting agent in pesticide formulations [11], and as drug carrier in pharmaceutical formulations [12]. AOT associates in water to form micelles at low concentrations, and lyotropic mesophases, e.g., hexagonal or lamellar, at higher concentrations [2,13–15]. The critical micelle concentration (CMC) of AOT in water has been obtained from surface tension measurements to be 2.6 mM (1.18 wt.%) [15]. As the surfactant concentration increases above the CMC, but below 29%, AOT micelles grow from spherical to ellipsoid [2].

The self-assembly of surfactants in water is modulated by the presence of co-solutes [16–18]. In particular, the addition of cyclodextrins may affect the surfactant association because of their binding

interactions with surfactant hydrophobic tails to form inclusion complexes [19]. Cyclodextrins (CDs) are toroid shape supramolecules composed of  $\alpha$ -D-glucopyranoside units that form a macrocycle ring [20]. Native cyclodextrins and their derivatives find a number of applications in pharmaceutical, cosmetic, and food industries for encapsulation of hydrophobic or volatile actives in the formulations, in analytical chemistry as separating agents, and in catalysis [20–26]. The exterior of the cyclodextrin molecules is hydrophilic while the central cavity offers a hydrophobic environment which is responsible for the binding of CD with surfactants.

Depending on the size of the central cavity and possible chemical modification, cyclodextrins form mainly 1:1, 2:1 or 1:2 CD:surfactant inclusion complexes with surfactants [19,27–33]. Specifically, the inclusion complexation of AOT with  $\alpha$ -cyclodextrin (6 member glucose ring),  $\beta$ -cyclodextrin (7 member glucose ring) and  $\gamma$ -cyclodextrin (8 member glucose ring) was examined using isothermal titration calorimetry [34] to suggest that AOT forms primarily 1:1 CD:AOT complexes with  $\alpha$ -,  $\beta$ - or  $\gamma$ -CD. The binding constant values of 170, 180, 490  $M^{-1}$  for 1:1 CD:AOT inclusion complexes of  $\alpha$ -CD,  $\beta$ -CD, and  $\gamma$ -CD, respectively [34], are lower compared to binding constants for 1:1 CD:surfactant complexation with the single-tail anionic surfactant sodium dodecyl sulfate (SDS) (21,000  $M^{-1}$  for 1:1  $\alpha$ -CD:SDS or  $\beta$ -CD:SDS complexation) [30], which can be attributed to lower hydrophobic

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interactions between the two hydrophobic, branched tails of AOT and the CD cavity compared to the single-tail interactions of SDS with the CD cavity [34]. Similar observations on the binding constants of  $\beta$ -cyclodextrin with AOT and other surfactants using conductivity measurements have been reported by Palepu et al. [35].

To the best of our knowledge, there are only two published studies on the complexation of cyclodextrins with AOT in aqueous solutions at AOT concentrations below the CMC [34,35]. The effects of CD–AOT binding in water at AOT concentration higher than CMC have not been explored yet. Several questions need to be addressed: How does cyclodextrin binding affect the micelle size, shape and interactions? How does the cyclodextrin type affect the AOT micelles? The answer to these questions can be obtained by probing AOT–cyclodextrin solutions using a structural characterization technique such as small-angle neutron scattering (SANS). In a recent study, we have utilized SANS to investigate CD effects on micelle formation and structure in aqueous SDS solutions [32,33]. SANS has been previously used for the characterization of aqueous solutions of AOT, either in the absence or in the presence of salt [2,13], however, SANS has never been used for studying AOT micelles in the presence of cyclodextrins.

The major objective of this work is to investigate using SANS how the micelle properties and inter-micelle interactions of the representative double-tail surfactant AOT are affected by cyclodextrins in aqueous solutions. We first consider AOT–water solutions as a reference system. We then examine AOT–cyclodextrin–water solutions with two different types of cyclodextrins,  $\alpha$ -cyclodextrin ( $\alpha$ -CD) and hydroxypropyl  $\beta$ -cyclodextrin (HP- $\beta$ -CD), and compare their effectiveness. To the best of our knowledge, this is the first investigation of the AOT–cyclodextrin–water system above the CMC, and one of only three published studies on AOT–CD aqueous solutions.

## 2. Materials and methods

### 2.1. Materials

Sodium bis(2-ethylhexyl) sulfosuccinate was purchased from Sigma (St. Louis, MO).  $\alpha$ -Cyclodextrin and hydroxypropyl  $\beta$ -cyclodextrin were purchased from Aldrich (St. Louis, MO). Hydroxypropyl- $\beta$ -CD has been used in the present study due to its higher aqueous solubility compared to  $\beta$ -CD. The degree of substitution of hydroxypropyl groups for  $\beta$ -cyclodextrin was specified as 4.3 by the supplier. Heavy water ( $D_2O$ ) was purchased from Cambridge Isotope Laboratories (Tewksbury, MA). All chemicals were used as received.

Stock solutions of surfactant and of CD in  $D_2O$  were first prepared, and then mixed in appropriate ratios with each other and with  $D_2O$  to obtain the desired final concentration. Adequate time for equilibration was allowed. The concentration of AOT varied from 2 mM to 22.5 mM to cover a wide range of surfactant concentrations above the CMC but below the surfactant concentration where lyotropic liquid crystal phases form [2]. The concentration of  $\alpha$ -CD varied from 0 to 40 mM, while the concentration of HP- $\beta$ -CD varied from 0 to 20 mM, above which all micelles were disassembled for an AOT concentration of 12 mM.

### 2.2. SANS measurements and data reduction

SANS measurements were performed on the 30 m spectrophotometer (NG3) at the National Institute of Standards and Technology (NIST) in Gaithersburg, MD. Neutrons with 6 Å wavelength and wavelength spread  $\Delta\lambda/\lambda = 14.3\%$  were focused on the sample kept in a 4 mm quartz cell at  $25 \pm 0.1$  °C. Sample-to-detector distance = 2 m for all samples, covering the wave vector ( $q$ ) range  $0.01 \text{ \AA}^{-1} < q < 0.3 \text{ \AA}^{-1}$ . The beam time was 180 to 4800 s for each measurement. Scattering data were corrected for scattering originating from background, empty cell and detector sensitivity. Absolute scale intensity was obtained by normalizing the scattered intensity with a well characterized polystyrene/

deuterated polystyrene standard [32,36]. Absolute intensity data were then corrected for incoherent solvent scattering and analyzed using different models available in NIST-supplied analysis software. Reduced SANS data were fitted to appropriate models for form and structure factors (see next section) using the non-linear least square method with Levenberg–Marquardt algorithm to obtain physically appropriate values of the fitting parameters. The uncertainties in the fitting parameters are specified here as one standard deviation in the fitting coefficient and are calculated from the fitting function of IGOR PRO [31].

### 2.3. SANS data analysis: micelle structure and interactions

The core–shell oblate ellipsoid form factor [2,13] and the Hansen–Hayter structure factor [37,38] are used in our study as the most appropriate in describing the scattering behavior of sodium bis(2-ethylhexyl) sulfosuccinate micelles in aqueous solutions.

The overall scattering intensity  $I(q)$  is given by Eq. (1):

$$I_{\text{micelle}}(q) = A \cdot \phi \cdot P(q) \cdot S(q) + B_{\text{inc}} \quad (1)$$

The form factor  $P(q)$  represents the shape and structure of a micelle (Fig. 2), while the structure factor  $S(q)$  represents the inter-micelle interactions and overall arrangement of micelles in the solution.  $\phi$  is the volume fraction of the micelles, which in turn depends on the overall surfactant concentration. The parameters  $A$  and  $B_{\text{inc}}$  are introduced to take into account additional contributions associated with absolute scaling and incoherent noise, respectively [32].

$P(q)$  was calculated using Eqs. (2) and (3) [32].

$$P(q) = \frac{1}{V_{\text{TOT}}} \int_0^1 |F(q, a, b, \delta, \beta)|^2 d\beta \quad (2)$$

$$F(q, a, b, \delta, \beta) = V_C(\rho_C - \rho_{\text{Sh}}) \frac{3j_1(u_C)}{u_C} + V_{\text{TOT}}(\rho_{\text{Sh}} - \rho_S) \frac{3j_1(u_T)}{u_T} \quad (3)$$

The first term in Eq. (3) represents scattering due to the core region of the micelle with core volume  $V_C = \frac{4\pi}{3} a^2 b$ , where  $a$  represents the major core radius and  $b$  represents the minor core radius. The second term in Eq. (3) signifies scattering due to the micelle shell region (with constant shell thickness  $\delta$  as shown in Fig. 2) of a micelle with volume  $V_{\text{TOT}} = \frac{4\pi}{3} (a + \delta)^2 (b + \delta)$ .  $j_1(u)$  is the first order spherical Bessel function of the first kind expressed by  $j_1(u_i) = (\sin u_i - u_i \cos u_i)/u_i^2$  where  $u_i = q [a_i^2 \beta^2 + b_i^2 (1 - \beta^2)]^{1/2}$ .  $\rho_C$ ,  $\rho_{\text{Sh}}$  and  $\rho_S$  are the scattering length densities of the micelle core, micelle shell, and solvent, respectively [32].  $\beta = \cos \mu$ , where  $\mu$  is the angle at which the major axis is inclined to the scattering vector  $q$ . The use of the monodisperse micelle form factor described here is appropriate for the higher-than-CMC surfactant concentrations that we use, where micelle–micelle interactions are prominent, and the effects of polydispersity on the intra- or inter-particle structure factor are less pronounced [2,39].

The structure factor  $S(q)$  was calculated using the screened coulomb potential, with mean spherical approximation [38] and rescaling corrections for low volume fractions [37], given the micelle volume fraction, charge on a micelle, and ionic strength of the solution. Micelles are approximated as charged spheres of diameter  $\sigma_0$  interacting through ion-impenetrable dimensionless screened coulombic potential [40] and the solvent is considered as a continuum charge screening medium with inverse Debye length  $\kappa$  as described by the Debye–Hückel theory. Since  $\kappa\sigma_0 < 1$  (where  $\kappa$  is the inverse Debye length and  $\sigma_0$  is the effective diameter of the micelle) and the contact potential  $\gamma \exp(-\psi) \gg 1$  mV, application of ion-impenetrable (hard-core) potential based structure factor is valid in our study [40]. The effect of non-spherical shape on the structure factor can be neglected, i.e., the apparent structure factor  $S'(q) = S(q)$  with  $\beta'(q) = 1$  where  $S'(q) = 1 + \beta'(q)[S(q) - 1]$  and

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