**SUMMER SCHOOL 2014 – NG3 HANDOUT**

**TEMPERATURE EFFECT ON THE NANOSTRUCTURE**

**OF SDS MICELLES IN WATER**

**INTRODUCTION**

Surfactants are amphiphilic molecules that form micelles in aqueous medium. The hydrophilic charged head groups associate with water while the hydrophobic tails aggregate inside the micelle core. Many investigations used characterization methods such as scattering or microscopy in order to study micelle structures. ~~Small-angle neutron scattering (SANS) studies from sodium dodecyl sulfate (SDS) micelles in water were conducted using mixtures of deuterated and non-deuterated surfactant molecules as well as end-deuterated molecules. Contrast variation series yielded micelle size, shape and aggregation number. Selective deuteration of the methyl groups gave insight into the packing of the micelle core [1]. Another SANS study of SDS micelle structure in water was conducted [2] in which the concentration and temperature dependences of the aggregation number were obtained. Lithium and sodium dodecyl sulfate (LDS and SDS) micelle formation in water was investigated upon LCl or NaCl salt addition. The aggregation number was found to increase with salt addition. NaCl was found to be more effective at screening Coulomb interactions than LiCl [3].~~

In another study, differential scanning calorimetry was used to determine the phase diagram for the SDS/water system [4]. The critical micelle formation (temperature and concentration) conditions were mapped out using calorimetry. The critical micelle concentration (CMC) of SDS in water was found to correspond to 0.2 % mass fraction which is equivalent to a molarity of 0.008 mol/L. ~~For the studied SDS mass fraction range above 30 %, hydrated SDS crystals were observed below 25~~ ~~o~~~~C. Cubic, hexagonal and lamellar phases along with a number of mesophases in-between were observed respectively for increasing SDS fractions. The hydrated SDS crystals observed at low temperatures melt to form micelles when temperature is increased. The Kraft point (corresponding to the intersection of the CMC with the crystal solubility limit) was found to be located around 10~~ ~~o~~~~C. In yet another study, cryo-TEM images showed broad band-like aggregation of multiconnected threads forming at the air-solution interface as well as cylindrical micelles in the bulk of the solution. Small size micelles were found at high temperature and low SDS fraction while more extended structures were found at low temperature and high SDS fraction [5]. Sodium alkyl sulfates mixed surfactants form micelles just like each of the individual pure surfactants in solution. SANS measurements pointed to spherical and ellipsoidal micelle particles. The aggregation number for the mixed surfactant micelles lies closer to that for the longer chain surfactant. Moreover, the fractional charge of the mixed micelles was found to be smaller than that for each single-component [6]~~

SANS was also used to examine the structure of micelles formed of pure SDS or pure dodecyltrimethylammonium bromide (DTAB) in aqueous solution [7]. Micelles were found to be of oblate ellipsoidal shape. Using model fitting, minor and major axes sizes were determined. Upon addition of NaBr salt, a disk-to-tablet transition was observed. Salt effect seems to stretch the micelles into sheets. The short dimension scales with the size of the SDS hydrocarbon chain. Another investigation focused on mixtures of SDS and DTAB in aqueous solution with salt addition [8]. Interesting structures were uncovered. Unilamellar vesicles, then oligolamellar vesicles, then lamellar sheet structures were observed with increasing surfactant fraction. Another more recent study looked at SDS/DTAC (chloride) surfactant mixtures instead with added salts [9]. Similar results were found for DTAB or DTAC. Using bromide or chloride ions does not make much difference. Specific ionic salts were added to mimic the surfactant head groups in order to investigate the competition between simple ionic screening and ionic binding (attachment to the micelle surface). In another study, SDS was used to coat carbon nanotubes in order to enhance their solubility and prevent their aggregation [10].

Focus in the present paper is on the use of the SANS technique to investigate the structure of pure SDS micelles in aqueous medium and follow micelle changes with SDS fraction and sample temperature; a broader range in SDS fraction and sample temperatures were measured.

**SAMPLES AND CHARACTERIZATION METHOD**

Sodium dodecyl sulfate (SDS) surfactant (99 % purity) was purchased from Sigma-Aldrich (St. Louis, USA) and D2O (d-water) was purchased from Cambridge Isotope Labs (99.9 % purity). A series of SDS solutions were prepared for small-angle neutron scattering (SANS) measurements. Samples with the following SDS mass fractions were prepared: ~~0.1 %, 0.5 %, 1 %, 2 %,~~ 5 %, ~~10 %, and 20 %~~.  ~~Three more samples were prepared where NaCl salt fraction was varied (0.1 mol/L, 0.2 mol/L and 0.5 mol/L) for the 1 % SDS/d-water sample.~~ Samples were allowed to equilibrate overnight.

SANS measurements were made using the NG3 30 m SANS instrument at the NIST Center for Neutron Research. Temperature was varied between 10 oC and 90 oC with 10 oC intervals. In practice, the heating system lags behind slightly so that the actual measured sample temperatures are: 11 oC, 21 oC, 30 oC, 40 oC, 49 oC, 59 oC, 68 oC, 78 oC, and 87 oC. Standard overhead runs such as from the empty cell, the blocked beam as well as sample transmission and empty cell transmission runs were taken. SANS data were scaled to an absolute cross section using the empty beam transmission method. Standard data reduction method was used in order to obtain radially averaged intensity (units of cm-1) as function of scattering variable Q (units of Å-1).

**TRENDS OBSERVED IN SANS DATA**

SANS data show a weak low-Q (long-range) feature and a dominant intermediate-Q (shorter-range) feature which is due to the micelle particles structure. The intermediate-Q peak and shoulder features observed in the SANS data are characteristic of anisotropic micelles such as ellipsoidal particles in agreement with previous results [7]. These are seen to move to higher Q (Figure 1) upon heating implying that particles get smaller with increasing temperature. The low-Q feature (observed at low SDS fractions) is likely due to clustering and characterizes water-soluble (especially ionic) systems. It has been discussed in the literature [11, 12]. It is characteristic of mass fractals (Porod exponents between 2 and 3).



Figure 1: SANS data for 5 % SDS mass fraction while varying temperature. The peak and shoulder features are characteristic of ellipsoidal micelles.

**SCATTERING MODEL**

The recurring clues characterizing the SANS data consist of two size scales observed on the intermediate-Q peak. This points to ellipsoidal shape micelles as reported previously for similar systems [6, 9]. A scattering model consisting of a solution of interacting ellipsoidal particles is used to fit the SANS data. The scattering cross section is expressed as:

**.** (1)

Here 2 is the contrast factor,  is the particle volume fraction, VP is the particle volume, P(Q) is the single-particle form factor, and SI(Q) is the inter-particle structure factor. This model works best for spherical particles, and is used here for ellipsoidal particles that are not too distorted.

The form factor represents an average over orientations of the anisotropic particles. It involves the following integral:

. (2)

Here  has been defined where  is the angle between the main axis of the ellipsoid and the  direction. Particles are assumed to be ellipsoidal with half axes Ra and Rb. For an oblate ellipsoid particle (with Rb>Ra), an effective radius Re is defined as:

. (3)

The form factor amplitude is the same as the one for a sphere of radius Re:

. (4)

Here  is the spherical Bessel function of order 1. Note that the orientations of single particles are assumed to be decoupled (valid for not too distorted particles and not too high particle fraction). With this caveat, the Mean Spherical Approximation (MSA) is used to model the structure factor ****. This model is known to be reliable when screened Coulomb interactions are present (such as for ionic micelles), and relies on the MSA closure relation to solve the Ornstein-Zernike equation [13]. It should be mentioned that the approximate MSA model is often used since it relies on an analytical solution whereas other more elaborate (numerical) solutions are available. Fits to this model yield effective sizes.

The following model parameters are used:  is the dielectric constant, D is the micelle (also called macroion) effective diameter,  is the Debye-Huckel inverse screening length, and zme is the electric charge on the micelle surface where e is the electron charge.

The Debye-Huckel screening parameter (inverse length) squared is expressed as follows:

 (5)

 and  are the micelle particle and salt volume fractions,  and  are the particle and salt molecule volumes, and kBT is the sample temperature in absolute units.

The micelle volume fraction  is expressed in terms of the number density  and micelle volume  as .

The MSA formalism used to derive the structure factor [13] is not reproduced here. This model is included in small-angle scattering data analysis software packages such as the IGOR-based package used at the NIST Center for Neutron Research. [14].

Note that the MSA model was originally introduced for spherical particles and is used here for ellipsoidal particles. This approximate approach should be reliable when the intermicelle distance is large compared to the micelle size.

In order to perform fits to the SANS data when sample temperature was varied, tabulated temperature dependence of the dielectric constant for d-water [15] is used (i.e., is fixed to help the fits).

Table 1: Temperature dependence of the dielectric constant for d-water

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Temp.  (o C) | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 |
| Dielectric Const.  | 83.526 | 79.755 | 76.161 | 72.427 | 69.470 | 66.358 | 63.391 | 60.561 | 57.875 |

**SANS DATA ANALYSIS**

The model used to fit the SANS data consists of the sum of two functional forms: a low-Q power law function and the ellipsoidal micelles model:

. (6)

n is a low-Q Porod exponent,  was discussed above and B is a constant representing the Q-independent background mostly due to incoherent scattering from hydrogen.

Smearing of the model was performed first using the SANS instrument resolution function. Then nonlinear least-squares fits were performed on all SANS data sets. Fitting was reasonable in most cases despite the large number of fitting parameters. The resulting model parameters are: the low-Q scale factor A and Porod exponent n, the micelles volume fraction fit, the ellipsoidal micelles half axes Ra and Rb, the scattering length density inside the micelles m, the scattering length density for the solvent s, and the charge on the micelles. The sample temperature in absolute units was also fixed as well as the dielectric constant for d-water [15]. The contrast factor involves the difference  where m and s are the micelles and solvent scattering length densities respectively. Note that only this relative difference is relevant here.

A typical fit is shown in Figure 5 for the 5 % SDS mass fraction sample at 49 oC. The model used to fit reproduces the low-Q power law feature as well as hugs the intermediate-Q curve representing the oblate ellipsoidal micelles. The low-Q clustering feature is observed in most water-soluble systems [11,12].

**SUMMARY AND DISCUSSION**

The research focused on an old topic and reported new results. The SDS surfactant forms micelle structures in aqueous medium. Micelle particles were found to be mostly of an oblate ellipsoidal shape (compressed spheroid). Nonlinear least squares fits to an appropriate model corresponding to non-dilute mixtures of oblate spheroids yielded estimates for the minor and major micelle half axes. ~~The 1 % SDS sample at 40~~ ~~o~~~~C, for example, is characterized by half axes of 14.1±0.1 Å and 20.9±0.1 Å respectively. These sizes are comparable with the previously reported dimensions of 12.0 Å and 20.3 Å for the same system [7]. At the highest SDS fraction of 20 % and lowest measured temperature of 11~~ ~~o~~~~C, another phase was observed. The two characteristic clues of a Bragg peak at high-Q and a strong low-Q signal point to hydrated SDS crystals in agreement with the published phase diagram [4].~~

The estimated micelle ellipsoid volume was found to decrease with increasing temperature ~~and/or decreasing SDS fraction~~. Moreover, the micelle charge was also found to decrease with increasing temperature ~~and/or decreasing SDS fraction as it should.~~

~~The oblate ellipsoid micelles half axes were found to increase with increasing NaCl salt addition. The minor half axis increases slightly then flattens out at 15 Å beyond 0.1 mol/L salt while the major half axis keeps on increasing up to 33 Å for 0.5 mol/L salt. The minor size is comparable to the SDS hydrocarbon tail size (fully extended size around 17 Å). Salt addition seems to screen charges on the micelles surface thereby allowing micelles to grow laterally while remaining of the thickness of one SDS close-to-stretched molecule.~~

~~The fitted micelle volume fraction ~~~~fit~~ ~~scales with the sample mixing SDS volume fraction ~~~~mix~~ ~~except at low (lower than 0.5 %) and high (higher than 10%) fractions. In the intermediate region around 1 % SDS fraction, it was concluded that not all SDS molecules participate in micelle formation; a small fraction remains homogeneously dissolved. In order to estimate that fraction and to assess whether any water gets into the micelle core, material balance equations were derived. The discrepancy between ~~~~fit~~ ~~and ~~~~mix~~ ~~as well as the fitted scattering length density difference between the micelle core and the solvent  are used as inputs in order to back out the SDS fraction participating in micelle formation. For the 1 % SDS sample, at least 80 % of the SDS molecules are found to participate in micelle formation. The remaining 20 % are used to keep the dissolved SDS close to the CMC level. Moreover, no water was found inside the micelle core region. The micelles aggregation number (number of SDS molecules per micelle) was found to decrease with increasing temperature and with decreasing SDS fraction. This scales well with the observed variation of the micelle volume and surface charge.~~

The reported results are in agreement with other findings in the literature. New results include detailed characterization of the micelle structure and its variation with temperature, ~~mass fraction and salt content. A set of material balance equations was introduced and found to be important for the understanding of subtle changes in the micelle content. Such material balance equation may prove to be important in characterizing hydration in globular proteins.~~

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Figure 5: Typical model fit and SANS data for the 5 % SDS/d-water sample at 49 oC.

Both ellipsoidal micelles half axes Ra and Rb decrease with increasing temperature as shown in Figure 6. The value of Rb was systematically larger than Ra pointing to oblate (i.e., compressed) ellipsoidal micelles as expected [7,10].