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.

Differential scanning calorimetry was used to determine the phase diagram for the SDS/water system [1]. The critical micelle formation (temperature and concentration) conditions were also mapped out. 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.

SANS was also used to examine the structure of micelles formed of pure SDS in aqueous solution [3]. 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 [4]. 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 [5]. 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 [6].

A recent paper focused 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 [12].

SAMPLES AND CHARACTERIZATION METHOD

Sodium dodecyl sulfate (SDS) surfactant (99 % purity) was purchased from Sigma-Aldrich (St. Louis, USA) and D_2O (d-water) was purchased from Cambridge Isotope Labs (99.9 % purity). A 5 % SDS in d-water was prepared for small-angle neutron scattering (SANS) measurements and was 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 [3]. 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 [7, 8] and is characteristic of mass fractals (Porod exponents between 2 and 3).

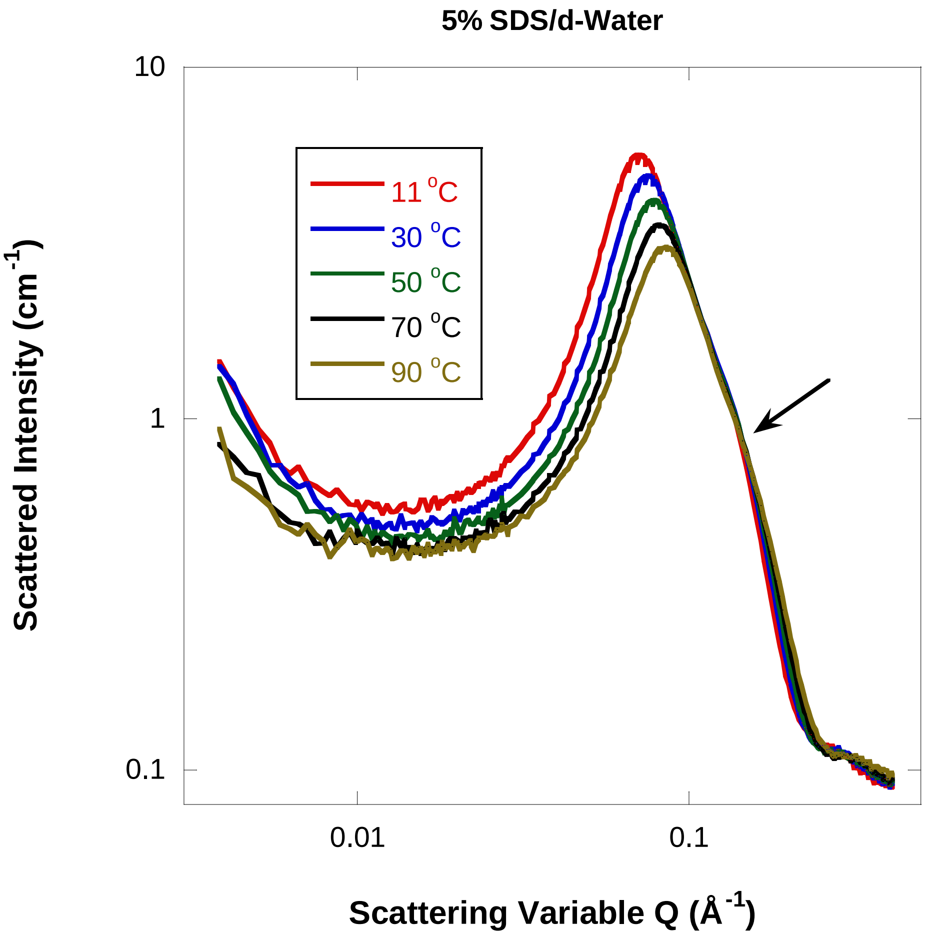

Figure 1: SANS data for 5 % SDS mass fraction while varying temperature. The peak and shoulder features are characteristic of ellipsoidal micelles.

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 [2, 5]. 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:

$$\left[\frac{d\Sigma(Q)}{d\Omega}\right]_{\text{ellipsoids}} = \Delta\rho^2 \phi V_P P(Q) S_I(Q). \qquad (1)$$

Here $\Delta\rho^2$ is the contrast factor, ϕ is the particle volume fraction, V_P is the particle volume, P(Q) is the single-particle form factor, and $S_I(Q)$ 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:

$$P(Q) = \frac{1}{2}\int_{-1}^{+1} d\mu P(Q,\mu) . \qquad (2)$$

Here $\mu = \cos(\theta)$ has been defined where θ is the angle between the main axis of the ellipsoid and the $\vec{Q}$ direction. Particles are assumed to be ellipsoidal with half axes R_a and R_b. For an oblate ellipsoid particle (with R_b>R_a), an effective radius R_e is defined as:

$$R_e^2 = R_b^2 + \mu^2 (R_a^2 - R_b^2) . \qquad (3)$$

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

$$P(Q,\mu) = \left[\frac{3 j_1(QR_e)}{QR_e}\right]^2 . \qquad (4)$$

Here $j_1(QR_e)$ 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 $S_I(Q)$. 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 [9]. 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: ε is the dielectric constant, D is the micelle (also called macroion) effective diameter, κ is the Debye-Huckel inverse screening length, and $z_m e$ 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:

$$\kappa^2 = \frac{e^2}{\varepsilon k_B T}\left(z_m \frac{\phi}{V_P} + \frac{\phi_{salt}}{V_{salt}} \right) \qquad (5)$$

ϕ and ϕ_{salt} are the micelle particle and salt volume fractions, V_P and V_{salt} are the particle and salt molecule volumes, and $k_B T$ is the sample temperature in absolute units.

The micelle volume fraction ϕ is expressed in terms of the number density $\overline{N}$ and micelle volume $V_P = \pi D^3/6$ as $\phi = \overline{N} V_P$.

The MSA formalism used to derive the structure factor [9] 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. [10].

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 [11] 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. ε	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:

$$I(Q) = \frac{A}{Q^{n}} + \left[\frac{d\Sigma(Q)}{d\Omega}\right]_{\text{ellipsoids}} + B. \qquad (6)$$

n is a low-Q Porod exponent, $[d\Sigma(Q)/d\Omega]_{\text{ellipsoids}}$ 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 ϕ_{fit}, the ellipsoidal micelles half axes R_a and R_b, the scattering length density inside the micelles ρ_m, the scattering length density for the solvent ρ_s, and the charge on the micelles. The sample temperature in absolute units (i.e., degrees K) was also fixed as well as the dielectric constant for d-water [11] given in Table 1. The contrast factor involves the difference $\Delta\rho^2 = (\rho_m - \rho_s)^2$ where ρ_m and ρ_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 ^{o}C. 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 [7,8].

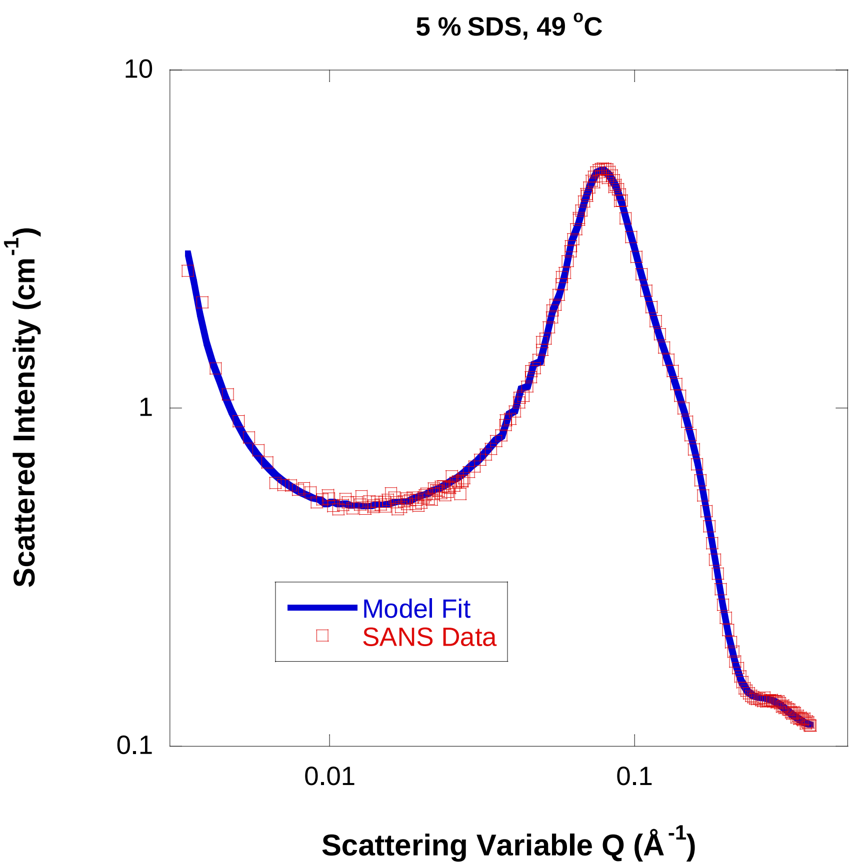

Figure 5: Typical model fit and SANS data for the 5 % SDS/d-water sample at 49 ^{o}C.

Both ellipsoidal micelles half axes R_a and R_b decrease with increasing temperature as shown in Figure 6. The value of R_b was systematically larger than R_a pointing to oblate (i.e., compressed) ellipsoidal micelles as expected [3,6].

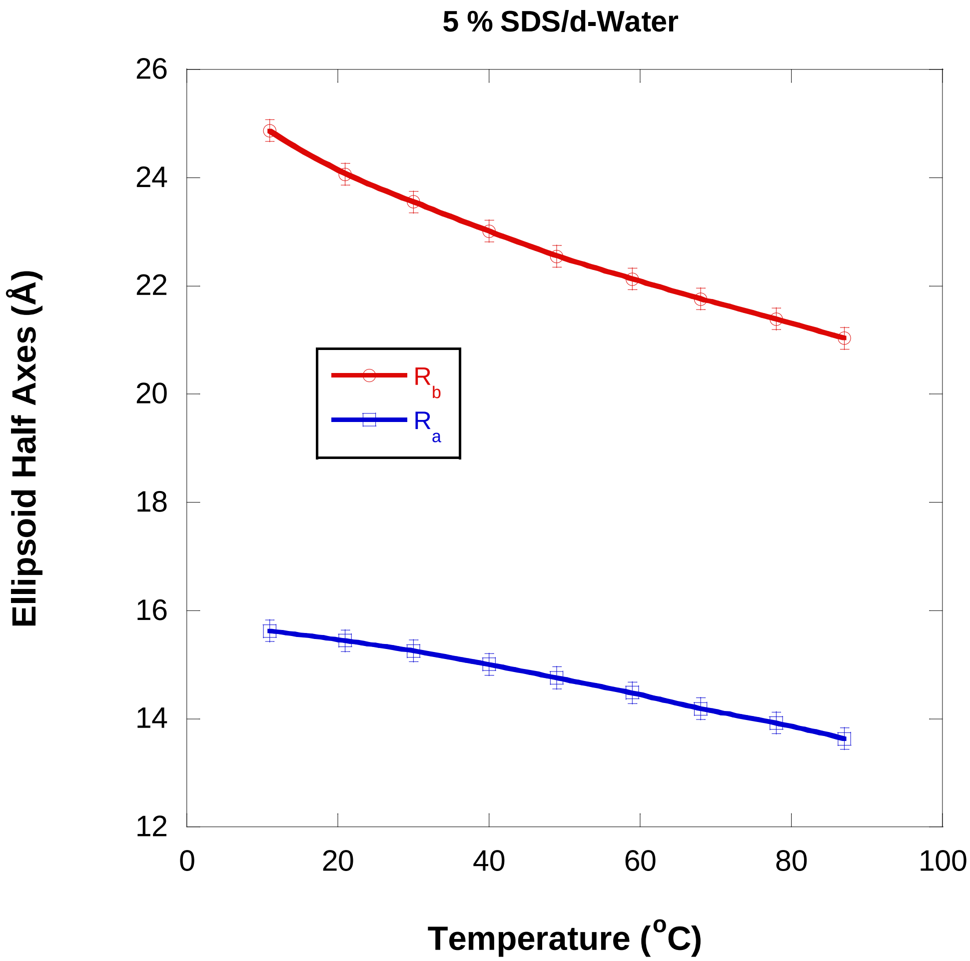

Figure 6: Variation of the ellipsoid micelles half axes with increasing temperature for the 5 % SDS sample. The lines going through the points are guides to the eye (smooth fitting).

The ellipsoidal micelle (oblate scattering particle) volume is estimated as $V_P = 4\pi R_a R_b^2 / 3$. This volume is seen (in Figure 7) to decrease consistently with increasing temperature. As temperature increases, the micelle volume decreases (so does the aggregation number) thereby yielding more (smaller) micelles. This is likely due to many factors that include softening of hydrogen-bonding of water molecules to the surfactant headgroups and packing of the surfactant tails.

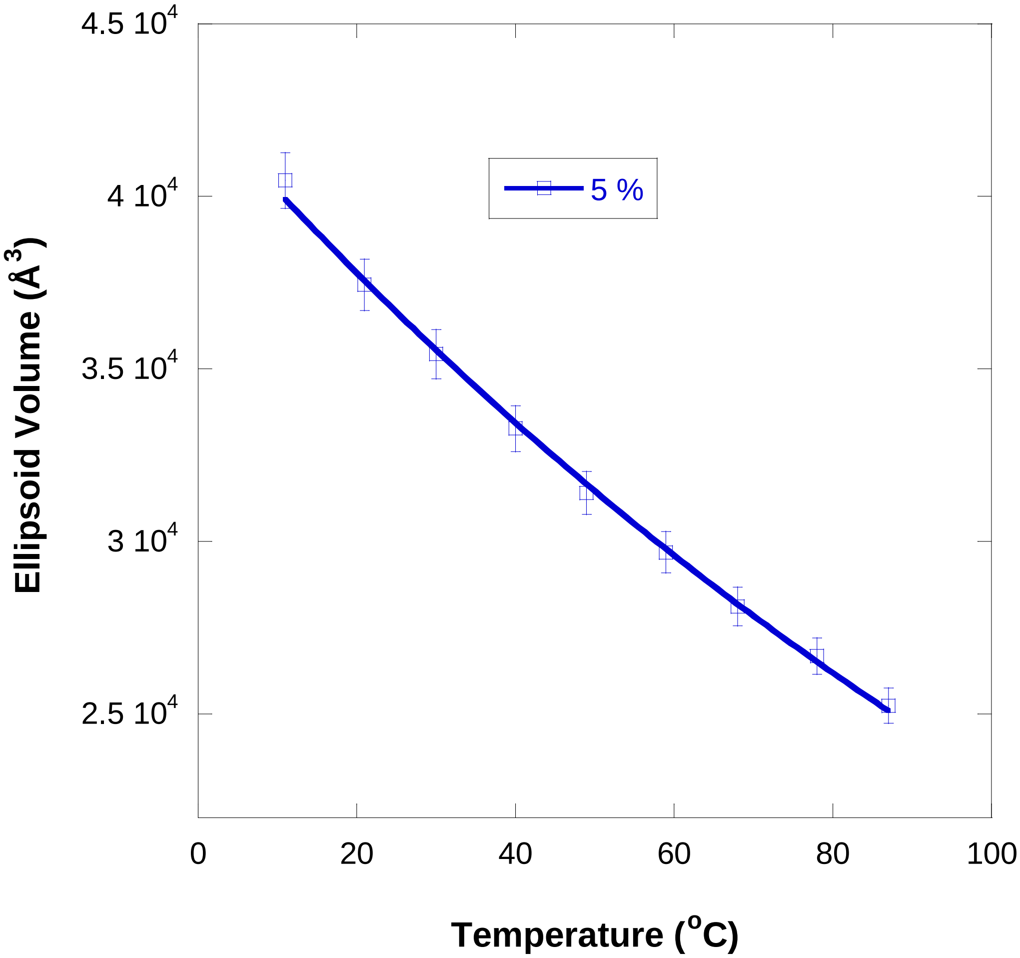

Figure 7: Variation of the ellipsoid micelle volume with increasing temperature.

Micelle charges, however, decrease with increasing temperature since the micelle volume decreases with increasing temperature.

SUMMARY AND DISCUSSION

This research focused on an old topic but 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 estimated micelle ellipsoid volume was found to decrease with increasing temperature. Moreover, the micelle charge was also found to decrease with increasing temperature as it should. 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.

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