SUMMER SCHOOL 2016 – NGB30 SANS HANDOUT

EFFECT OF ETHANOL COSURFACTANT ON SDS MICELLES NANOSTRUCTURE

INTRODUCTION

Surfactants are amphiphilic molecules that form micelles in aqueous medium. They are used extensively as detergents, emulsifying and foaming agents and dispersants among others. Surfactants constitute a simple template to investigate self-assembling systems. The hydrophilic charged head groups associate with water at the micellar surface 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.

Sodium dodecyl sulfate (SDS) surfactants have been the subject of many investigations. 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.

Small-angle neutron scattering (SANS) was used to examine the structure of micelles formed of SDS in aqueous solution [2]. Micelles were found to be of oblate ellipsoidal shape. Using model fitting, minor and major axes sizes were determined. The short dimension scales with the size of the SDS hydrocarbon chain.

A previous study focused on the use of the SANS technique to investigate the structure of SDS micelles in d-water (deuterated water) and follow changes in micellar nanostructure with SDS fraction and sample temperature [3]; a broader range in SDS fractions and sample temperatures were measured. That investigation for instance concluded that SDS remains dissolved in water at the critical micelle formation level even above the critical micelle fraction (CMC). Another finding using results from fits to SANS data along with a set of material balance equations concluded that no water can be found inside the micelles. The effect of adding d-ethanol (deuterated ethanol) co-surfactant on the SDS micelles nanostructure is investigated here. Using deuterated solvents enhances the neutron contrast.

SAMPLES AND SANS MEASUREMENTS

SDS surfactant (99 % purity) was purchased from Sigma-Aldrich (St. Louis, USA) and D_2O (d-water) and d-ethanol were purchased from Cambridge Isotope Labs (99.9 % purity). Samples with 5 % SDS fraction dissolved in a range of d-water/d-ethanol solvent mixtures were prepared for small-angle neutron scattering (SANS) measurements and were allowed to equilibrate overnight. This series corresponded to a range between 0% d-ethanol/100 % d-water and 80% d-ethanol/20 % d-water. Fine mesh points corresponding to 1 %, 3 %, 5 %, 8 % and 10 % d-ethanol were taken at low d-ethanol fraction then large meshes corresponding to 20 %, 40 %, 60 % and 80 % d-ethanol spanned the rest of the range. Since SDS does not dissolve in pure d-ethanol, the 100 % d-ethanol/0 % d-water sample was not measured.

SANS measurements were made using the NGB30 30 m SANS instrument at the NIST Center for Neutron Research. For the measurements in pure d-water, temperature was varied between 10 ^{o}C and 90 ^{o}C with 10 ^{o}C intervals. For measurements in d-water/d-ethanol mixtures, temperature was varied between 10 ^{o}C and 50 ^{o}C. In practice, the heating system lags behind slightly so that the actual measured sample temperatures are: 11 ^{o}C, 21 ^{o}C, 30 ^{o}C, 40 ^{o}C, 49 ^{o}C. 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 $Å^{-1}$).

SANS DATA FOR 5 % SDS IN PURE WATER

SANS data show a weak low-Q (long-range) feature and a dominant intermediate-Q (shorter-range) feature which has information about the micelle particles structure [3]. 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 [2]. These are seen to move to higher Q (Figure 1) upon heating implying that micelles 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 [4, 5] and is characteristic of mass fractals (Porod exponents between 2 and 3).

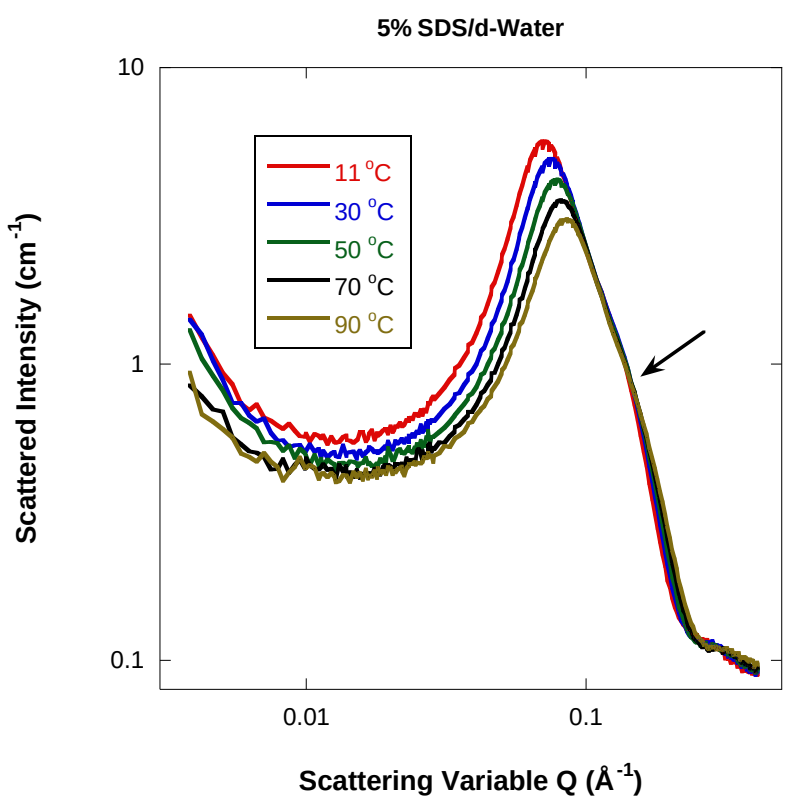

Figure 1: SANS data for 5 % SDS mass fraction in pure d-water with varying temperature. The peak and shoulder features are characteristic of ellipsoidal micelles.

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. 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 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 [6]. 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 respectively, 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 [6] 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. [7].

The dielectric constant for d-water is 78 while that for d-ethanol is lower (24.3) at 25 ^{o}C. Since the fit results for the micellar size are not very sensitive on the dielectric constant, tabulated temperature dependence of the dielectric constant for d-water [8] is used (i.e., is fixed to help the fits).

Table 1: Dielectric constant ε for ethanol/water mixtures

	Ethanol Fraction	1.0	0.80	0.60	0.40	0.20	0.10	0.0
Temp (^{o}C)								
10		26.68	39.0	51.92	64.53	75.02	80.45	84.13
20		25.07	36.98	48.93	0.96	71.23	76.67	80.37
30		23.5	34.80	46.2	57.69	67.72	73.13	76.75
40		21.97	32.8	43.73	54.72	64.49	69.83	73.27
50		20.48	30.94	41.52	2.05	61.54	66.77	69.93

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:

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

n is a low-Q Porod exponent, $[d\Sigma(Q)/d\Omega]_{ellipsoids}$ 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 (fixed), 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 [8] 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 °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 [4,5].

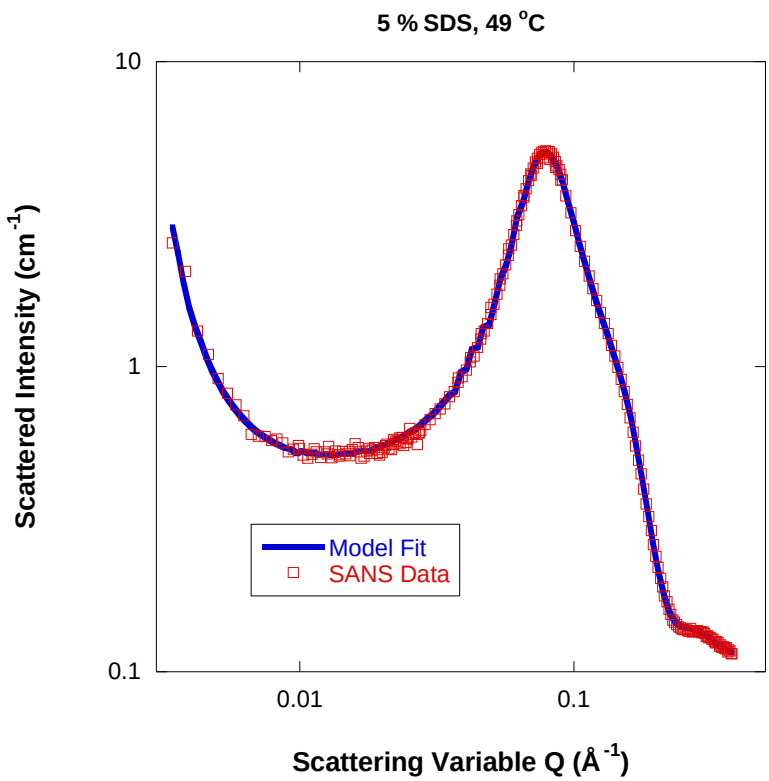

Figure 2: Typical model fit and SANS data for the 5 % SDS/d-water sample at 49 °C.

Both ellipsoidal micelles half axes R_a and R_b decrease with increasing temperature as shown in Figure 3. The value of R_b was systematically larger than R_a pointing to oblate (i.e., compressed) ellipsoidal micelles as expected [2].

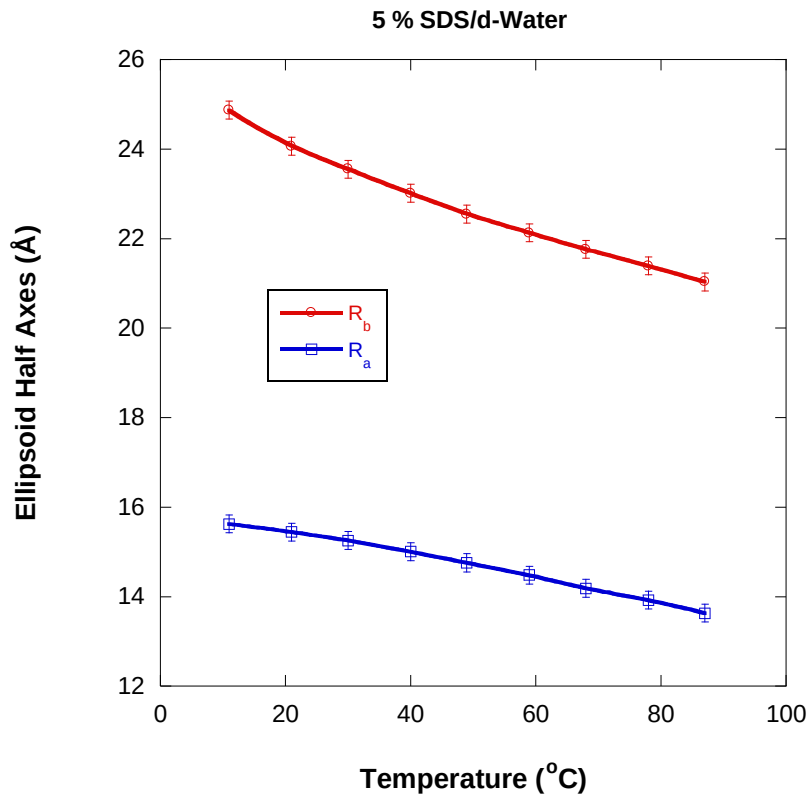

Figure 3: Variation of the ellipsoid micelles half axes with increasing temperature for the 5 % SDS sample. The lines going through the points are guides to the eye (smooth fitting).

The ellipsoidal micelle (oblate scattering particle) volume is estimated as $V_P = 4\pi R_a R_b^2/3$. This volume also decreases 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 head groups and packing of the surfactant tails.

SANS DATA FOR 5 % SDS IN D-ETHANOL/D-WATER MIXTURES

When the d-ethanol co-surfactant fraction is increased, the intermediate-Q peak becomes weaker and moves to higher Q as shown in Figure 4. This means that micelles become smaller and less well-formed.

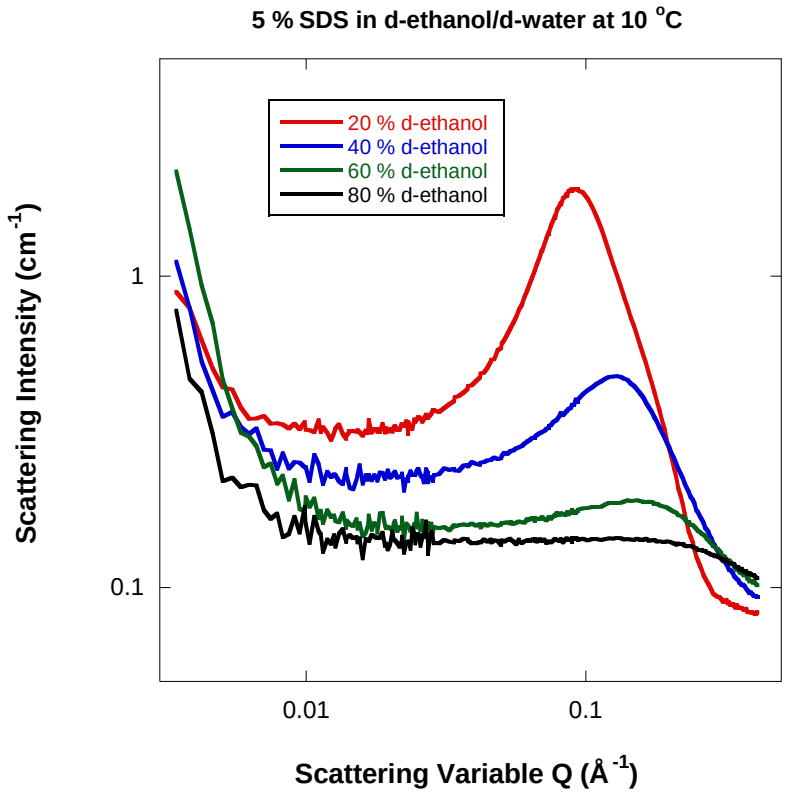

Figure 4: SANS data for 5 % SDS in d-ethanol/d-water mixtures at 10 ºC with varying fraction of d-ethanol in the solvent.

Fits of SANS data in this mixed solvent series to the same model described above yielded the following results. The half axes representing the ellipsoidal micelles decrease with increasing d-ethanol fraction (Figure 5). The ellipsoid starts as a clearly oblate and ends up closer to a sphere at high d-ethanol fraction.

The micellar volume decreases with increasing d-ethanol fraction in the mixed solvent (Figure 6).

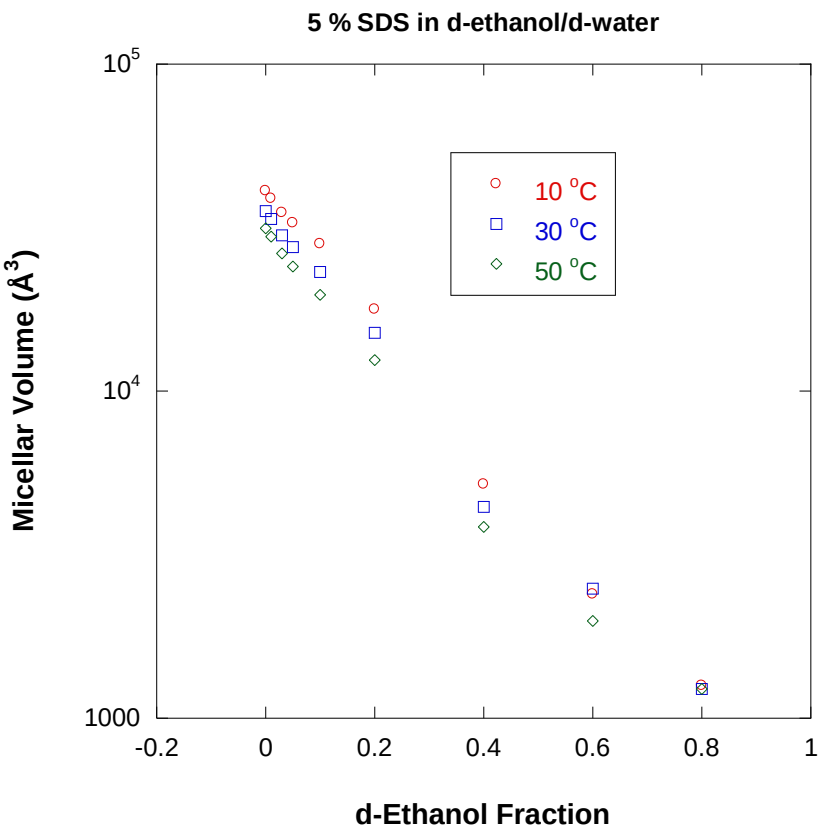

Figure 5: Variation of the micellar volume with increasing d-ethanol fraction in the solvent for three sample temperatures.

The charge on the micellar surface also decreases with increasing d-ethanol fraction (Figure 7).

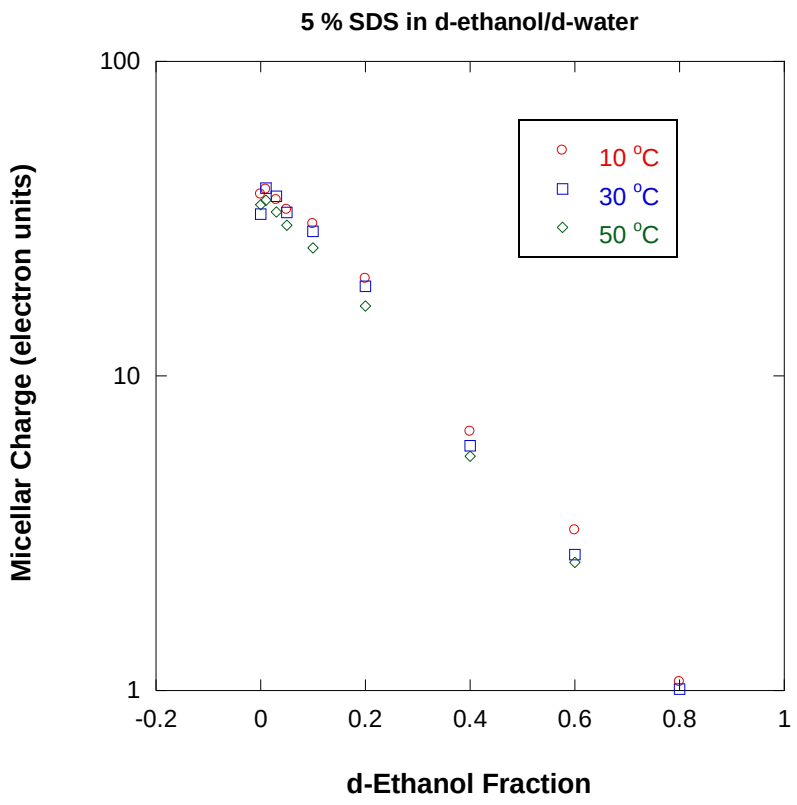

Figure 6: Variation of the charge on the micellar surface with increasing d-ethanol fraction in the solvent for three sample temperatures.

During the fits, the scattering length density (sld) for the solvent was fixed. For pure d-water, the sld corresponds to $6.39*10^{-6}$ Å^{-2} while for pure d-ethanol, it is $6.15*10^{-6}$ Å^{-2}. These rather close values are to be compared to that for SDS which is $0.287*10^{-6}$ Å^{-2}. The fit results for the micelles sld are plotted in Figure 8. Limiting values for pure SDS and pure d-ethanol are also marked on the figure. As the amount of d-ethanol is increased, the micelles sld increases which means that micelles contain more and more d-ethanol. It is fortunate that SDS is "hydrogenated" (small sld) while d-ethanol is deuterated (high sld) so that intake of d-ethanol is clearly observed. The carbon tail of d-ethanol (CD_3CD_2-) is hydrophobic and is expected to resides in the interior of the micelles while the hydroxy group (-OD) resides at the surface.

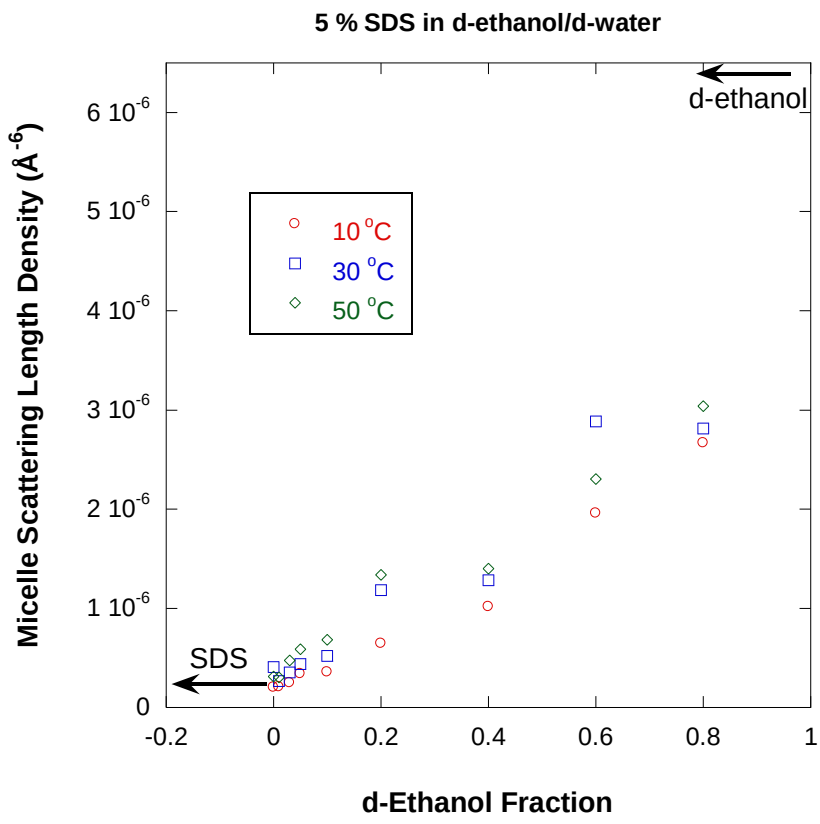

Figure 7: Variation of the scattering length density inside the micelles with increasing d-ethanol fraction in the solvent for three sample temperatures.

Using the micelles sld, one can estimate the relative fraction of d-ethanol in the micelles (Figure 9). One can see that with 80 % d-ethanol in the solvent mixture, as much as 45 % of the micelle content consists of d-ethanol. This is a surprising but significant result.

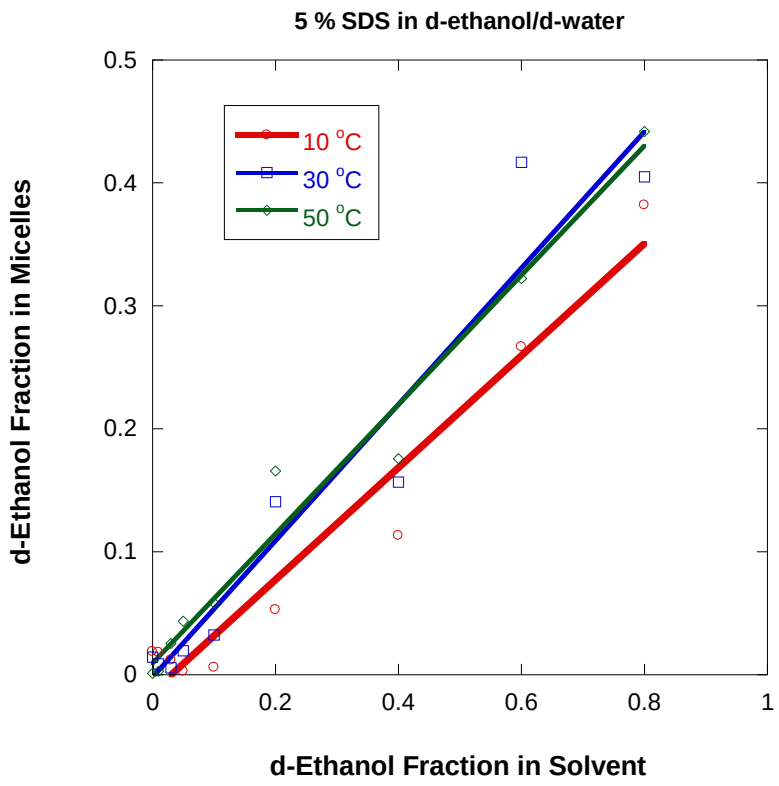

Figure 8: Variation of the d-ethanol fraction in the micelles (obtained from the scattering length density) with increasing d-ethanol fraction in the solvent for three sample temperatures. A linear fit line was added.

CONCLUSIONS

This research focused on an old topic but reported new results. The SDS surfactant forms a micellar structure 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. For SDS in pure d-water, the estimated micelle ellipsoid volume and surface charge were found to decrease with increasing temperature. When d-ethanol co-surfactant is added, micelles become smaller and more spherical. An interesting trend change from oblate ellipsoid to spherical micelles was observed. Moreover, micelles absorbed great deal of the d-ethanol co-surfactant. This is a significant result attesting to the amazing value of the SANS technique.

Ethanol/water mixtures behave differently than the individual solvents. When mixed together, these two solvents may form complex cage-like structures. Since these structures are not crystalline, crystallography cannot be used to resolve them. Such cage-like solvation structures form around synthetic polymers as well as around bio-macromolecules. SANS can only give a hint as to the solvation ability of ethanol/water mixtures. Most water-soluble polymers obey a co-solvation rule whereby solvent mixtures are better at dissolving polymers than the individual

ones. One exception to the rule is PNIPAM which obeys a co-nonsolvation rule whereby ethanol/water mixtures prompt the polymer to demix completely in the mid-window range (50%/50% ethanol/water mixtures) while it dissolves perfectly in pure ethanol and in pure water [9].

Resolving the cage-like ethanol/water structures would have wide-reaching consequences toward better understanding of solvation phenomena as well as of thermodynamic mixing/demixing.

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