Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


## Supplementary Information

# SANS Characterization of Time Dependent, Slow Molecular Exchange in SDS Micellar System

*Tooba Shoaib*[1], *Jae-Min Ha*[2], *Youngkyu Han*[3], *Wei-Ren Chen*[1] *and Changwoo Do*[1*]

[1]Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, 37831, Tennessee, United States
[2]Samsung Electronics, Hwaseong, Gyeonggi 18448, Republic of Korea
[3]Basic Research & Innovation Division, Amorepacific Corporation R&D Center, Yongin 17074, Republic of Korea

[*] Correspondence to doc1@ornl.gov

**KEYWORDS.** SDS micelle, surfactant molecular exchange, Time-resolved small-angle neutron scattering

**Table of contents**

- **Figure S5.** SAXS data of h-SDS, d-SDS, and mixed SDS showing no structural effect by isotope replacement.
- **Derivation for exchanged area based approach**

**Table S1.** Molecular weight, density and SLD of the components of the surfactant and solvent mixtures.

| | Mw | Density | SLD |
|---|---|---|---|
| h-SDS | 288.38 g/mol | 1.01 g/ml | 3.40E-07 $Å^{-2}$ |
| d-SDS | 313.53 g/mol | 1.10 g/ml | 5.83E-06 $Å^{-2}$ |
| NaCl | 58.44 g/mol | 2.17 g/ml | 2.95E-06 $Å^{-2}$ |
| $H_2O$ | 18.02 g/mol | 0.997 g/ml | -5.60E-07 $Å^{-2}$ |
| $D_2O$ | 20.03 g/mol | 1.107 g/ml | 6.36E-06 $Å^{-2}$ |

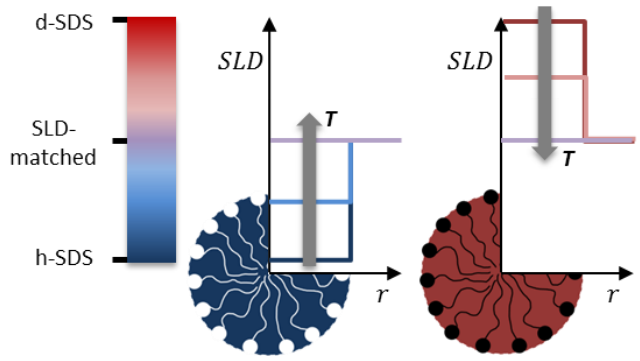



**Figure S1.** Schematic summarizing the change in SLD for deuterated (red) and protonated (blue) SDS micelles as a function of time. Given enough time, both types of micelles are fully randomized resulting in micelles comprising of an equal number of d-SDS and h-SDS surfactant molecules. At this ratio, the SLD of randomized micelles is completely matched with the SLD of the solvent.

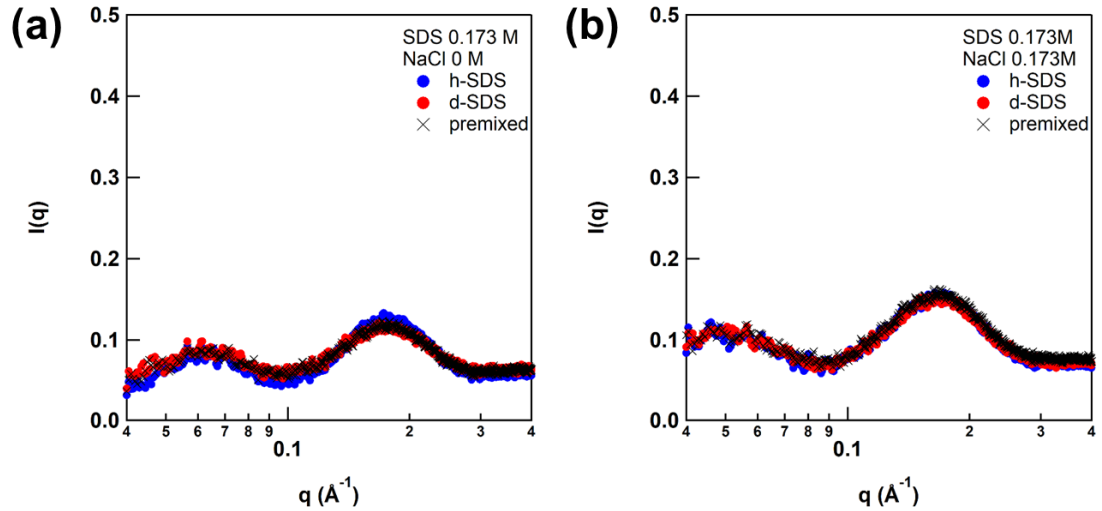



**Figure S2.** Small-angle x-ray scattering (SAXS) intensities of (a) the SDS (0.173 M) aqueous solutions without NaCl and (b) the SDS (0.173 M) aqueous solutions with NaCl (0.173 M).

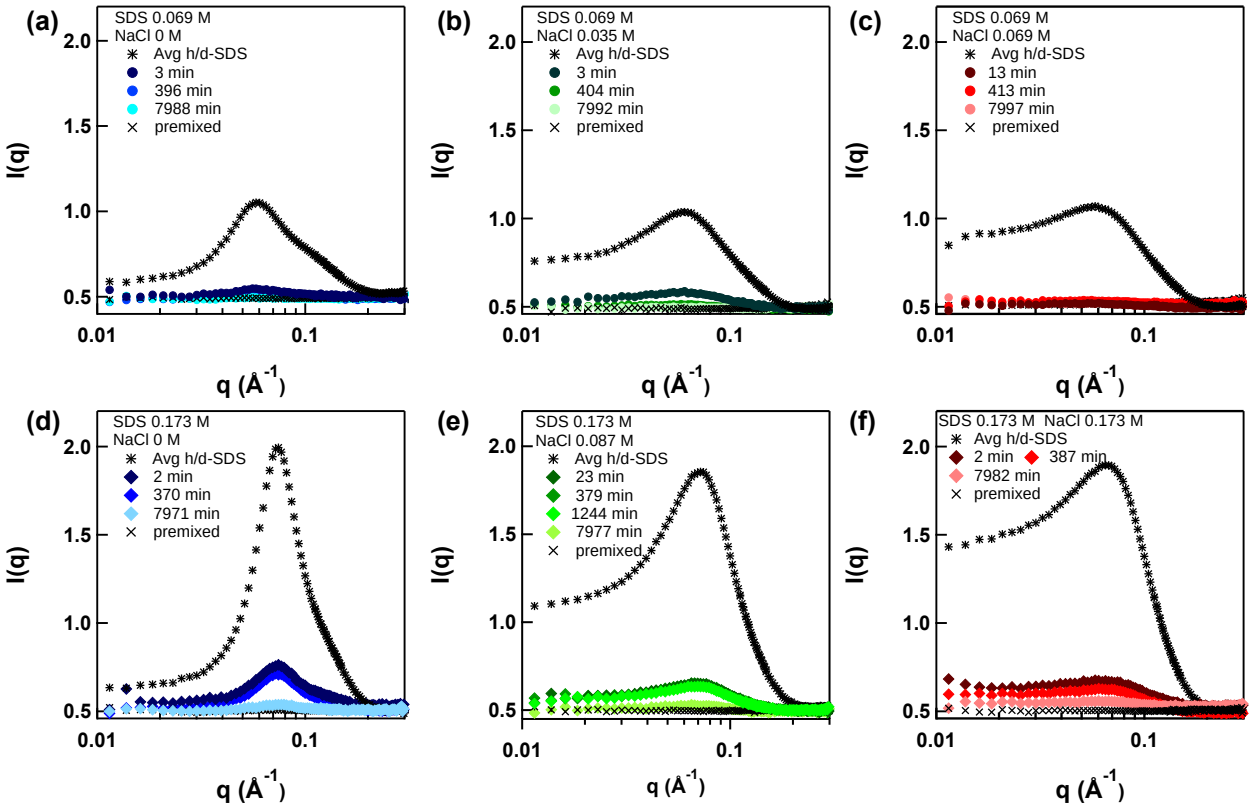



**Figure S3.** Static SANS averaged intensity from h-SDS and d-SDS and TR-SANS measurements at selected times for all SDS-NaCl solutions.

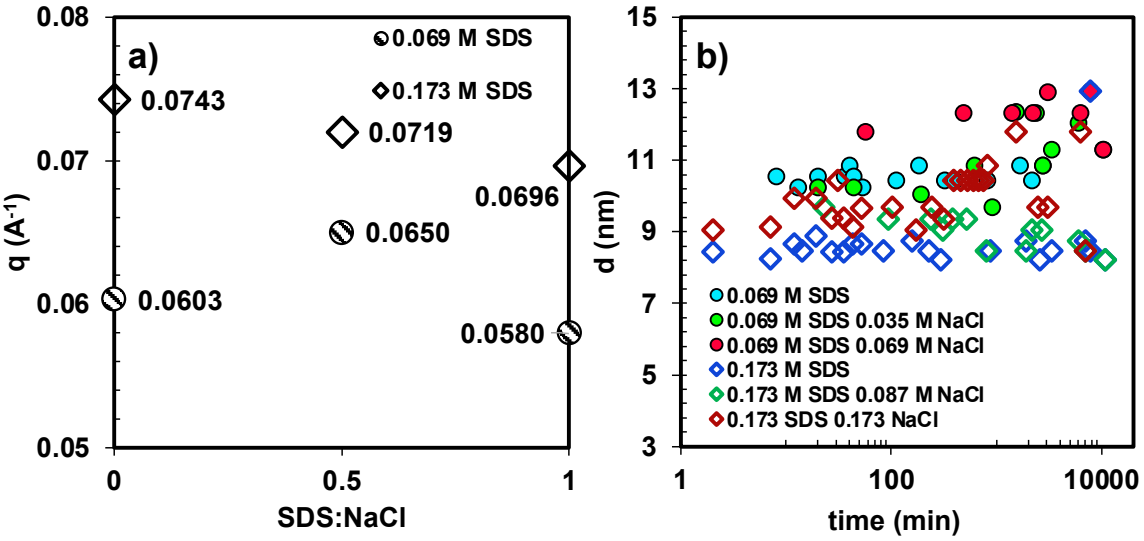



**Figure S4.** (a) The interaction peak position as a function of the surfactant to salt ratio. (b) The interparticle distance as a function of time for the 6 different solutions of SDS

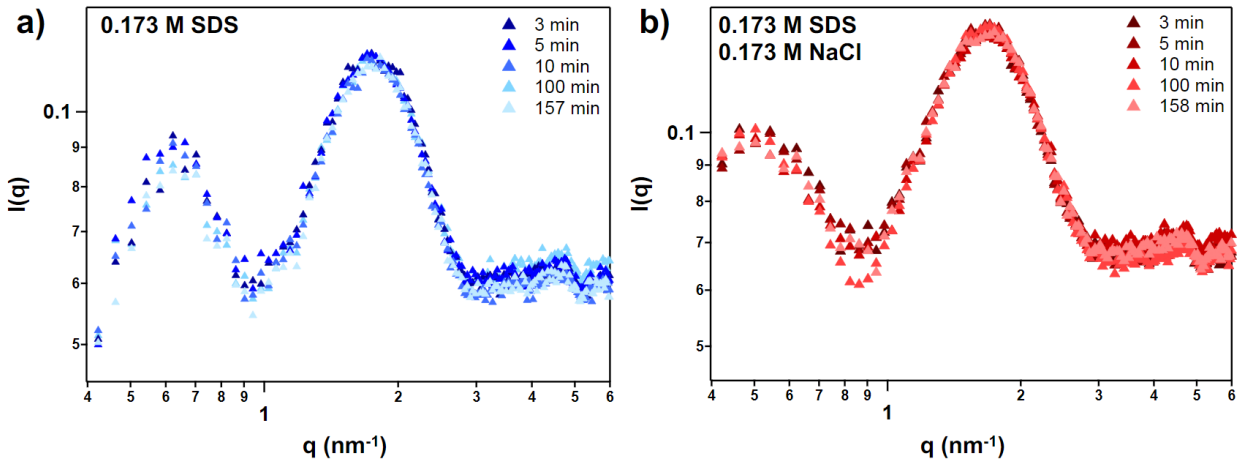



**Figure S5.** SAXS data for 0.173 M h/d-SDS solutions with a) no salt and b) 0.173 M NaCl measured as a function of time. No change in the scattering occurs as the micelles undergo randomization upon mixing of the d-SDS and h-SDS.

**Derivation for exchanged area based approach**

$$I(q) = n_m \Delta\rho_m^2 v_m^2 P(q) S(q) + I_{inc}$$

where $n_m$ is the micellar number density, $\Delta\rho_m$ is the difference of the SLD between micelle and solvent, $v_m$ is the volume of a SDS micelle, and $P(q)$ is the form factor related to the intra-micellar correlation, $S(q)$ is the structure factor regarding the spatial distribution of micelles in solutions, and $I_{inc}$ is the incoherent scattering (flat background at high q region).

During the molecular exchange, we assume that there are only three kinds of micelles such as d-SDS, h-SDS and fully exchanged SDS micelles (denoted by *exch*) to reduce the complexity for understanding the micellar exchange dynamics.

$$I(q) = n_{d-SDS} \Delta\rho_{d-SDS}^2 v_{d-SDS}^2 P(q) S(q) + n_{h-SDS} \Delta\rho_{h-SDS}^2 v_{h-SDS}^2 P(q) S(q) + n_{exch} \Delta\rho_{exch}^2 v_{exch}^2 P(q) S(q) + I_{inc}$$

The $P$(q), $S$(q) as well as $v_m$ for the d-SDS, h-SDS, and *exch* micelles are exactly the same, which are supported by SAXS measurement (Figure S2). Considering that the micelle number density is the function of time, the I(q) can be reorganized as:

$$I(q,t) = [n_{d-SDS}(t) \Delta\rho_{d-SDS}^2 + n_{h-SDS} \Delta\rho_{h-SDS}^2 + n_{exch}(t) \Delta\rho_{exch}^2] v_m^2 P(q) S(q) + I_{inc}$$

As shown in Figure 2 and 3, the *exch* micelles are invisible by neutrons, indicating that the neutron SLD difference between *exch* micelle and contrast matched solvent ($\Delta\rho_{exch}$) can be negligible. It should be noted that the neutron SLD of the exch micelles is corresponding to that of the middle point between h-SDS and d-SDS, which is suggesting that the $\Delta\rho_{h\text{-}SDS}$ is coincidence with the $\Delta\rho_{d\text{-}SDS}$.

$$I(q,t) = [n_{d-SDS}(t) + n_{h-SDS}(t)]\Delta\rho^2 v_m^2 P(q)S(q) + I_{inc}$$

Since $n_{d-SDS}(t) + n_{h-SDS}(t) = n_{total} - n_{exch}(t)$

$$I(q,t) = [n_{total} - n_{exch}(t)]\Delta\rho^2 v_m^2 P(q)S(q) + I_{inc}$$

The coherent scattering intensity is the scattering intensity excluded incoherent scattering as below

$$I_{coh}(q) = I(q) - I_{inc}$$

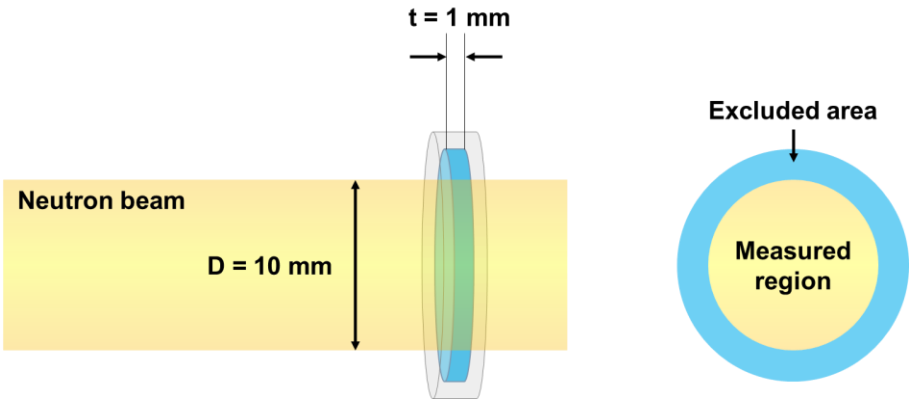
$$I_{coh}(q,t) = [n_{total} - n_{exch}(t)]\Delta\rho^2 v_m^2 P(q)S(q)$$

Then, the ratio between time-dependent $I_{coh}(q,t)$ and initial $I_{coh}(q,0)$ can be expressed by a number of micelles as a function of time.

$$\frac{I_{coh}(q,t)}{I_{coh}(q,0)} = \frac{[n_{tot} - n_{exch}(t)]\Delta\rho^2 v_m^2 P(q)S(q)}{n_{total}\Delta\rho^2 v_m^2 P(q)S(q)} = 1 - \frac{n_{exch}(t)}{n_{tot}}$$

From the neutron scattering experiment point of view, the micelle number density is

$$micelle\ number\ density\ [\#/cm^3] = \frac{micelle\ number\ within\ the\ neutron\ beam}{neutron\ beam\ path\ volume}$$




Since the neutron beam size is too large compared to the cell thickness, the exchange dynamics along the perpendicular direction for the cell cross-section are not significant (parallel direction to the neutron beam). Therefore, we assume that the SANS results related to exchange phenomena

are governed by the micellar exchange along the parallel direction to cell cross-section. Under the hypothesis, we estimated the degree of the micellar exchange by using the exchanged area-based calculation as below.

$$\frac{I_{coh}(t)}{I_{coh}(0)} = \frac{I_{coh}(t)}{I_{avg}} = \alpha(t)$$

The $\alpha(t)$ is proportional to the exchanged area and can be considered as the normalized area.