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Supporting Information Micelle Structure in a Deep Eutectic Solvent: A Small-Angle Scattering Study

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Small-angle scattering model test

Different models were tested to find the optimal choice. Our first selection of models was based on previous studies of self-aggregation of SDS in water and other solvents. Therefore sphere, ellipsoidal and cylindrical models with a core-shell cross section were tested for a micelle and a reverse micelle. A simple cylinder model was included in the test since it was the model used in our previously reported work.[1] Also a custom model composed of a core-shell cylinder form factor with a non-constrained hard-sphere structure factor was developed in order to fit the patterns in which the structure factor was appreciable. The Fig. S1 shows a SAXS pattern with the different models and the Table S1 includes the chi-square parameters for each fit.

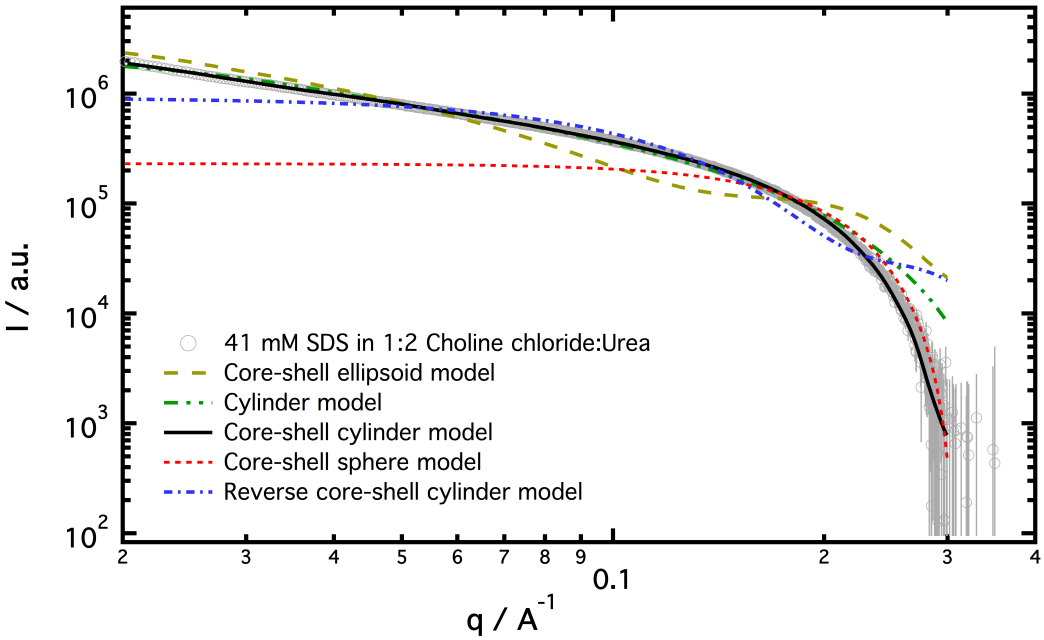

Fig. S1 Comparison of the best possible fits for different models for the 41.2 mM of SDS in choline chloride/urea DES.

Table S1 Chi-square values for the different models fitted to the data presented in Fig. S1. The chi-square corresponding the reverse core-shell structure was the best fit with positive values.

Model	Chi-square
Core-Shell cylinder	6.3
Cylinder	74.8
Reverse core-shell cylinder	1211
Core-shell ellipsoid	2115
Core-shell sphere	9637

After several tests at different concentrations and water contents, two different shape-dependent models were chosen to provide the best fits for the data across the concentration range measured. The core-shell cylinder model was used to fit the concentrations up to 42 mM. The samples with concentrations above this value were fitted to the custom model that includes the structure factor. The samples with water content were also fitted to this custom model.

Scattering length densities

The scattering length densities (SLD) of each solvent were calculated and kept constant during the fitting (Table S2). The SLDs of the micelle core, containing the surfactant tails, were calculated considering non-solvent penetration and a 12-carbon tail. The SLDs were calculated as the sum of the scattering lengths of each atom present in the system divided by the molecular volume of such molecule. These values were separately calculated for X-Rays and neutrons and afterwards kept constant during the fitting procedure in order to follow the changes in the structural parameters.

The shell SLD for X-Rays was fixed to a value which considers an arbitrary amount of solvent penetration, in agreement with our previous study.[1] Variations in this parameter were found to not affect the dimensions of the micelle core. Thus we believe that this approach provided a reliable approximation of the micelle core which was afterwards used during the analysis of neutron data. The surfactant counterion was considered to be solvated in the solvent, therefore non-contributing to the SLD of the shell. The neutron scattering length for the shell was included as a fitting parameter since the solvent adsorption would lead to different values depending on the contrast.

Table S2 X-Ray and neutron scattering length densities of each part in the system used in X-Ray and Neutron fits

	Neutron SLD / $\times 10^{-6}$ Å^{-2}	**X-Ray SLD / $\times 10^{-6}$ Å^{-2}**
h-choline chloride/h-urea	1.11	11.5
d-choline chloride/d-urea	6.56	-
h-choline chloride/d-urea	3.52	-
h-choline chloride/h-urea/H_2O	0.97	11.3
d-choline chloride/d-urea/D_2O	6.65	
h-choline chloride/h-urea/$2H_2O$	0.86	11.2
d-choline chloride/d-urea/$2D_2O$	6.71	
h-choline chloride/h-urea/$4H_2O$	0.68	11.0
d-choline chloride/d-urea/$4D_2O$	6.79	
SDS head group	-	12.6
h-C_{12}	-0.39	7.2
d-C_{12}	7.09	-

Small-angle X-ray scattering

For the X-Ray data, the patterns were fitted individually allowing the length, core-radius, shell-thickness, scale factor and S(q) volume fraction to vary. The background was considered as zero because the background contribution was proportionally subtracted from each pattern. Although small contributions may remain present, the addition of this extra variable did not produce any improvement in the fits.

The amount of information obtained from the X-Ray data was limited due the rather narrow q-range where the data was found to be acceptable. Scattering from the beamstop affected the measurement during the data acquisition (Fig. S2). This feature produces a pronounced increment on the scattering intensity at low q, and we were unable to reliably subtract this contribution or neglect it. Thus we decide to crop the data and limit our analysis to a small range of q. This issue clearly affects our analysis and does not allow us to

draw conclusions about the largest dimensions of our scatterers from the SAXS data alone. Nevertheless we believe that the scattering at high q remains unaffected and successfully fitted the cross-section of the micelles.

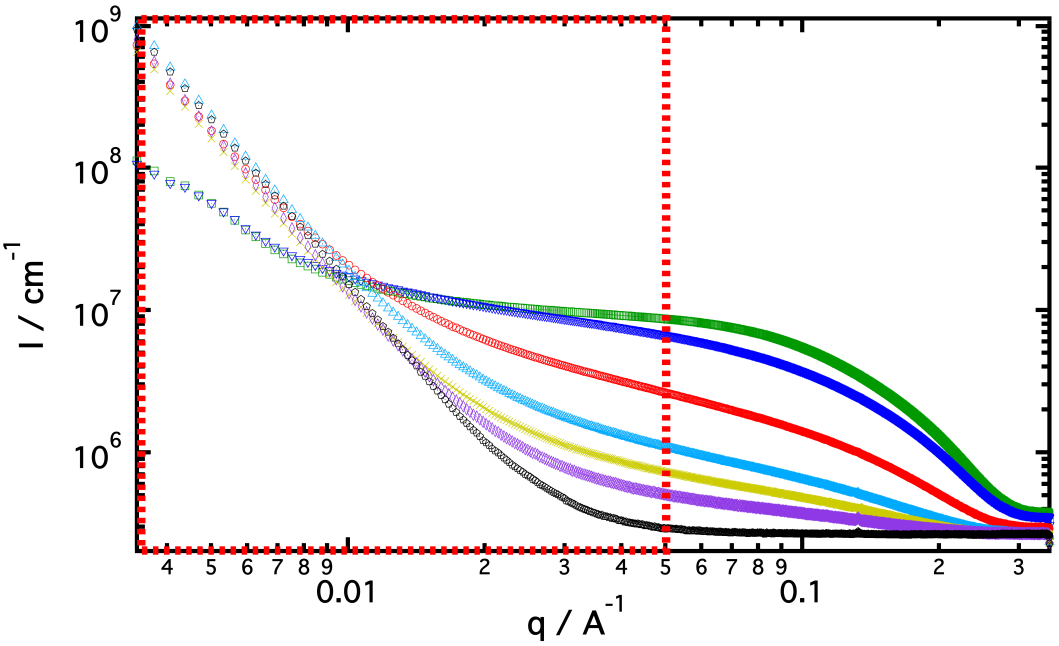

Fig. S2 High intensity signal in the SAXS pattern. The scattering from the beamstop was found to affect the signal between 3×10^{-3} and ~4×10^{-2}.

Small-angle neutron scattering

The small-angle neutron scattering data was fitted using the parameters obtained from the SAXS data as the first approach to the optimal fit. The scattered intensity in the SANS data was normalised in order to obtain it on an absolute scale. Hence the scale factor of the fitted curve actually corresponds to the volume fraction of the micelles.

Three different isotopic mixtures were simultaneously fitted to the two models explained above. The structure factor effect was found to be negligible below 42 mM of SDS in pure DES. Below this concentration the core-shell cylinder model was used to fit the SANS data. Above this concentration the model with the non-constrained structure factor was used to optimise the fits. In those cases, the value of the radius effect of the S(q) was held to 35 Å and the S(q) volume fraction fitted. The value of 35 Å was found to be an average of the interaction range when both parameters were fitted for different concentrations. Therefore we consider that it may be the best approach towards the analysis.

For the whole set, the core-radius, shell-thickness, length and S(q) volume fraction were fitted simultaneously as parameters that were identical between the three different contrasts. The volume fraction included in the form factor of the model was not constrained during the simultaneous fit. The slight differences between the concentrations of the contrasts appear in differences in this scale factor. Also SLD deviations, arising from the calculation of SLD due to the variability of this value with density, influence the discrepancy between these values. In order to validate this data all of the contrasts were individually fitted and averaged. Table SIII includes one of the concentrations with the three different fits, one for each contrast plus the simultaneous fit for comparison between these different methods of fitting. Both fitting approaches have shown to be in good agreement.

Table S3 Comparison between the individual fits, averaged fit and simultaneous fit of these three contrasts for an intermediate of concentration of SDS in 1:2 Choline chloride:Urea

Fit	Length (Å)	Shell-thickness (Å)	Shell SLD ($\times10^{-6}$ Å^{-2})	Volume fraction of micelles ($\times10^{-2}$)	S(q) volume fraction
Individual hh-solvent + 70.9 mM d-SDS	810±50	11.3±3.8	1.7±0.3	3.3±1.1	4.6±0.4
Individual dd-solvent + 93.2 mM h-SDS	323±1	9.5±0.3	6.0±0.3	3.0±0.1	2.9±0.1
Individual hd-solvent + 79.8 mM h-SDS	338±4	9.1±0.4	3.0±0.2	3.4±0.2	2.3±0.1
Average of individual fits	490±22	10±2	10±2	3.2±0.5	3.3±0.2
Simultaneous fit	328±12	10±1	hh-d 1.6±0.1 dd-h 6.1±0.1 hd-h 3.1±0.1	3.5±0.1	2.8±0.1

SANS data were therefore simultaneously fitted using the three contrasts. The Fig. S3 shows the plots for the 3 contrasts with the corresponding best fit for each concentration.

The Fig. S3 shows the SANS data and best fits for the three contrasts of the surfactant in the dry DES. The parameters used for each fit are contained in Table S4.

For the samples which contain water, the data was simultaneously fitted using two contrasts, d-SDS in 1:2:n h-Choline chloride:h-Urea:H_2O and h-SDS in 1:2:n d-Choline chloride:d-Urea:D_2O, with n=1, 2, 4. Table S5 includes the parameters of the best fit for each concentration of surfactant in the DES/water mixture

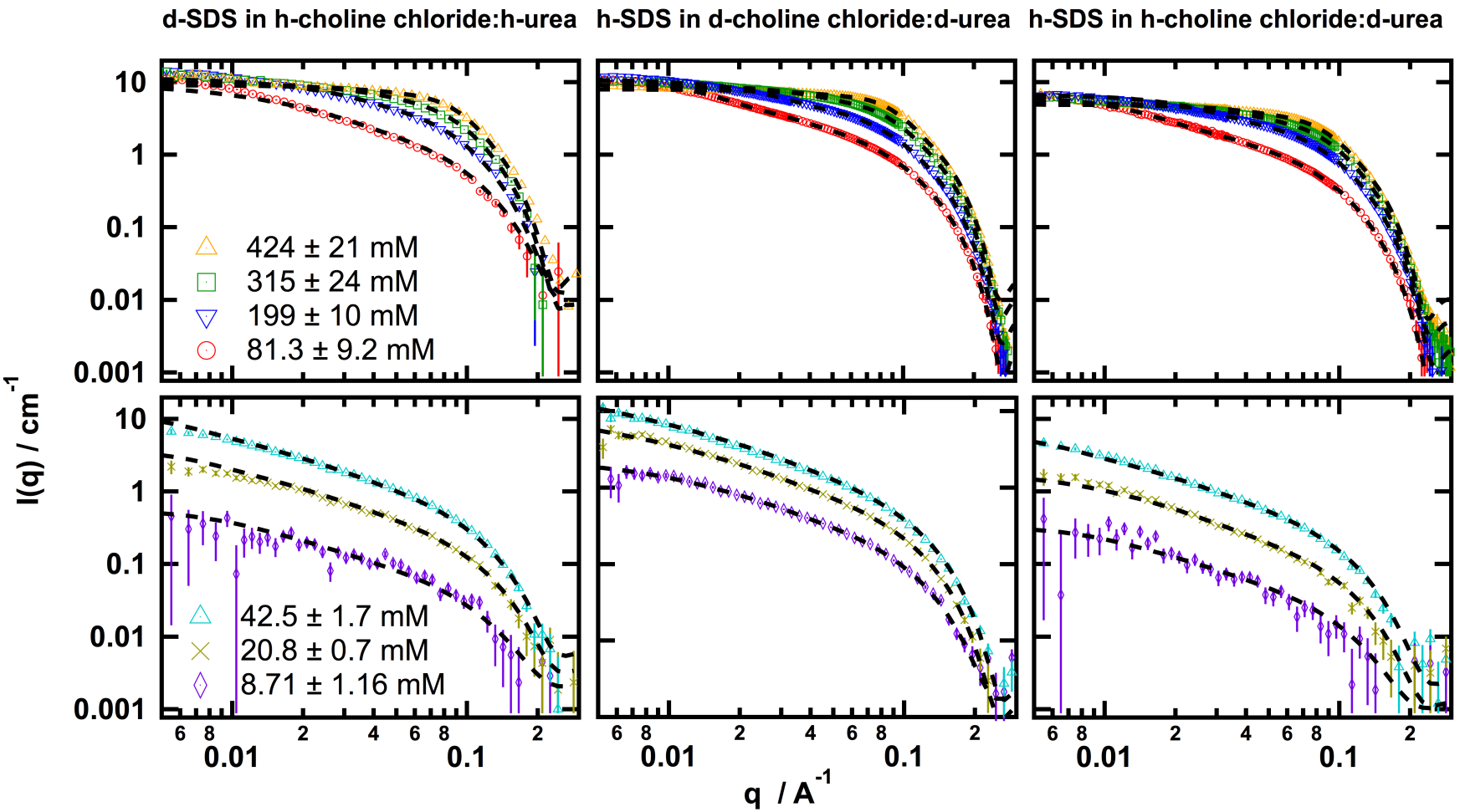

Fig. **S3** SANS data and co-refined fits of different concentrations of SDS for the three contrasts: (left) d-SDS in 1:2 h-Choline chloride:h-Urea, (middle) h-SDS in 1:2 d-Choline chloride:d-Urea, and (right) h-SDS in 1:2 h-Choline chloride:d-Urea. The average concentrations are shown in the plot in the left plots. The black-dashed lines correspond to the best fits obtained through the simultaneous fit of the three contrasts.

Table **S4** Fitted parameters of the SANS data of different concentrations of SDS in the three contrasts of dry DES.

Contrast	Concentration (mM)	Length (Å)	Shell-thickness (Å)	Shell SLD ($\times10^{-6}$ Å^{-2})	ϕ_{fit} ($\times10^{-2}$)	S(q) Volume Fraction ($\times10^{-2}$)
hh-d	8.71±1.16	414±39	5.6±0.4	1.4±0.1	0.10±0.04	0.1±0.5
dd-h				6.0±0.1		
hd-h				3.0±0.1		
hh-d	20.8±0.7	568±81	6.1±0.8	2.0±0.1	0.43±0.02	0.1±0.5
dd-h				5.3±0.1		
hd-h				2.6±0.1		
hh-d	42.5±1.7	668±28	7.4±0.4	2.2±0.1	1.3±0.1	0.2±0.5
dd-h				5.0±0.1		
hd-h				2.30±0.1		
hh-d	81.3±9.2	328±12	10±1	1.6±0.1	3.5±0.1	2.8±0.1
dd-h				6.1±0.1		
hd-h				3.1±0.1		
hh-d	194±10	176±4	8.4±0.2	2.5±0.1	6.7±0.1	5.1±0.1
dd-h				5.8±0.1		
hd-h				3.0±0.1		
hh-d	315±24	119±1	6.5±0.1	2.9±0.1	8.2±0.1	8.1±0.2
dd-h				5.6±0.1		
hd-h				2.6±0.1		
hh-d	424±21	108±1	4.7±0.1	3.2±0.1	9.6±0.1	12±1
dd-h				5.4±0.1		
hd-h				1.9±0.1		

Table **S5** Best-fit parameters for the SANS data of SDS in solvents containing water. The data and fits are included in Fig. 7 of the main text.

Contrast	Water mole equivalents	Length (Å)	Shell Thickness (Å)	Shell SLD ($\times10^{-6}$ Å^{-2})	ϕ_{fit} ($\times10^{-2}$)	S(q) Volume fraction ($\times10^{-2}$)
81.4 ± 10.8 mM						
hhh-d	1	270±1	5.3±0.2	2.9±0.1	2.1±0.1	2.3±0.1
ddd-h				5.7±0.1		
hhh-d	2	219±4	7.4±0.1	2.1±0.1	2.1±0.1	4.2±0.1
ddd-h				5.8±0.1		
hhh-d	4	117±1	6.7±0.1	2.1±0.1	2.1±0.1	8.7±0.1
ddd-h				5.7±0.1		
204 ± 15 mM						
hhh-d	1	174±1	8.4±0.1	1.6±0.1	7.7±0.1	5.5±0.1
ddd-h				6.0±0.1		
hhh-d	2	143±1	10±1	2.1±0.1	6.5±0.1	6.8±0.1
ddd-h				5.9±0.1		
hhh-d	4	121±1	6.9±0.1	2.2±0.1	6.0±0.1	8.7±0.1
ddd-h				5.6±0.1		
319 ± 22 mM						
hhh-d	1	121±1	6.6±0.1	2.1±0.1	10±1	8.7±0.1
ddd-h				5.6±0.1		
hhh-d	2	114±1	8.7±0.1	2.3±0.1	8.8±0.1	8.7±0.1
ddd-h				5.8±0.1		
hhh-d	4	116±1	7.0±0.1	2.1±0.1	9.1±0.2	10±1
ddd-h				5.8±0.1		

References

1. T. Arnold, A. J. Jackson, A. Sanchez-Fernandez, D. Magnone, A. E. Terry and K. J. Edler, *Langmuir*, 2015, **31**, 12894-12902.