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Counterion binding alters surfactant self-assembly in deep eutectic solvents

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Synthesis and characterisation of the counterion-exchanged surfactant

Protonated sodium dodecylsulfate (SDS, 99 %, Sigma) and lithium dodecylsulfate (LiDS, 99 %, Alfa Aesar) were purchased and used without further purification. Cesium dodecylsulfate (CsDS) and choline dodecylsulfate (ChDS) were prepared by counterion exchanging SDS and neutralisation of hydrogen dodecylsulfate with the corresponding hydroxide, caesium hydroxide (99.9 %, Alfa Aesar) and choline hydroxide (45 wt % aq. solution, Acros Organics). The organic acid hydrogen dodecylsulfate was prepared by exchanging the sodium counterion using ion exchange resin Amberlite IR120 (hydrogen form, Acros Organics) following the procedure explained by Lu *et al*.[1]

Magnesium didodecylsulfate ($Mg_{1/2}DS$) was prepared by direct mixing and precipitation from SDS and magnesium chloride anhydrous (>98 %, Sigma-Aldrich). 1 mole equivalent of magnesium chloride was dissolved at 60 ˚C and mixed with 2 mole equivalents sodium dodecylsulfate. After 2 hours the solution was removed from the heat and allow to cold down to 23 ˚C, thus $Mg_{1/2}DS$ selectively crystallised below its Krafft point.[2] The resulting solution was filtered and the white powder recovered. The product was subsequently recrystallized from Mili-Q water.

BmimDS and EmimDS were prepared according to the previously-described literature route.[3] Under stirring at room temperature in methanol, salt formation was performed by mixing equimolar sodium dodecylsulfate and either 1-butyl-3-methylimidazolium chloride or 1-ethyl-3-methylimidazolium chloride. The precipitate was filtered under gravity and the solvent removed *in vacuo*. The surfactant ionic liquid was purified by repeated centrifugation (3x20 minutes) in dry ethyl acetate with gravity filtration to remove remnant NaCl. Finally, the solvent was removed *in vacuo*, the surfactant dried, and the 1:1 ratio between cation and anion confirmed by NMR spectroscopy.

Deuterated versions of sodium dodecylsulfate (d-SDS), lithium dodecylsulfate (d-LiDS) and magnesium didodecylsulfate (d-$Mg_{1/2}DS$) were supplied by ISIS Deuteration Facility. Deuterated caesium dodecylsulfate was prepared from d-SDS following the same procedure as described above.

With the exception of the surfactant ionic liquids BmimDS and EmimDS which form polymorphic solids, all surfactants were purified following the procedure outlined by Weil.[4] $Mg_{1/2}DS$, CsDS and d-CsDS were triple-recrystallised from water and ethanol, and ChDS was recrystallised three times from ethanol/diethyl ether.

The purity of the surfactants was assessed by ^{1}H-NMR and sodium atomic absorption spectroscopy. An ionisation suppressant was added to the samples in order to minimise interferences within the sodium absorption spectrum. The purity of the counterion-exchanged surfactants was better than 98 % in all cases.

Samples for surface tension measurements of these surfactants in DES were prepared by dilution of stock solutions to reduce variability. A high concentration stock solution was prepared by direct mixing of each surfactant in the corresponding solvent. The solutions were equilibrated for at least 24 h at 50 ˚C and subsequently diluted down using the pure solvent to obtain a range of various concentrations below and above the CMC. These samples were sealed and stored under a dry atmosphere to prevent the adsorption of water from the environment.

Different concentrations above the CMC of each surfactant were prepared for SANS experiments by direct mixing of the DES with the surfactants. These samples were sealed and equilibrated in an oven at 40 ˚C overnight. After equilibration, samples were sealed and stored until the experiments were performed.

Surface tension of dodecylsulfate surfactants in choline chloride based DES

The surface tension of the various systems investigated here was measured using the pendant-drop method in order to find the CMC of those. Fig. S2 presents the surface tension data of the surfactants in choline chloride:urea and choline chloride:glycerol. The CMC values are included in the main text.

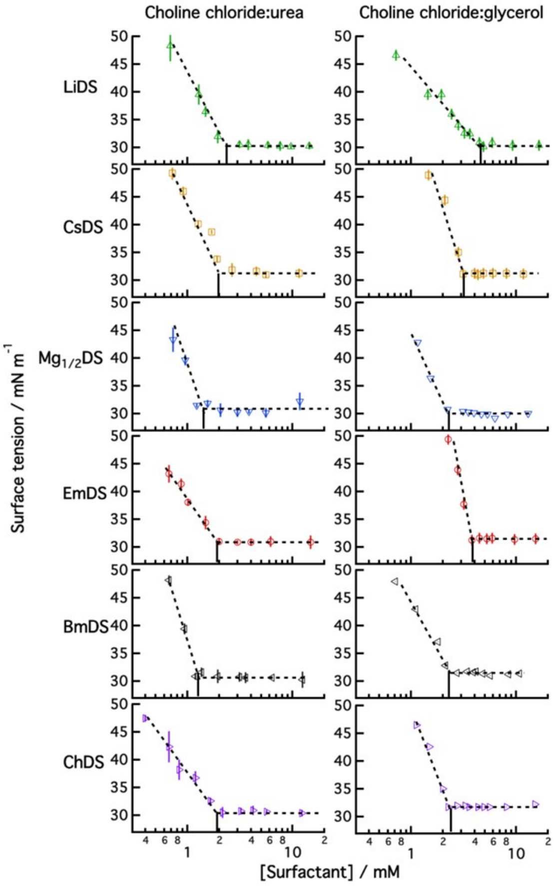

Fig. S1 Surface tension plots of different surfactants in choline chloride:urea and choline chloride:glycerol, as indicated in the graph. The black dashed lines represent the trends pre- and post-micellar regions and assist to find the CMC value.

Although sodium dodecylsulfate is not a part of this investigation, the ubiquity of such surfactant makes an excellent system for comparison with our results. The CMC of SDS in choline chloride:urea has been previously reported, however such value in choline chloride:glycerol has not been presented, to the best of our knowledge. Therefore we have measured the CMC of SDS in choline chloride:glycerol. The surface tension results *vs.* the concentration of SDS in choline chloride:glycerol is presented in Fig. S2.

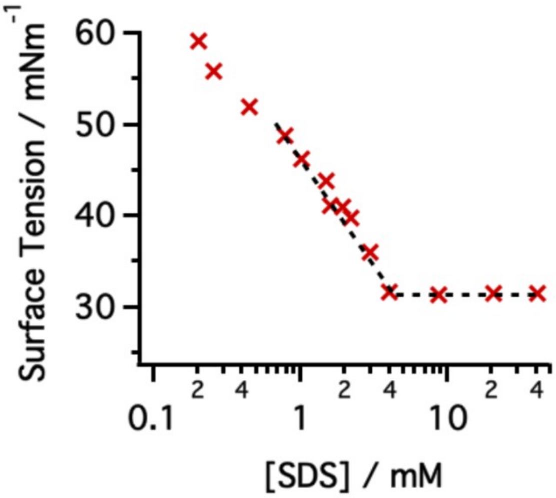

Fig. S2 surface tension of SDS in choline chloride:glycerol versus the concentration of surfactant. The CMC is obtained from the intersection of the two lines that describe the pre- and post-micellar regions.

The CMC of this system was found to be 3.9±0.1 mM, higher than the CMC of SDS in choline chloride:urea (CMC=2±1 mM)[5] but still lower than that in water (8.1 mM).[6]

Model test

Surfactant micelles may present various morphologies in solution. In order to find out the most likely micelle morphology, we have used different mathematical models to fit the experimental data. A comparison between different models was carried out for a low concentration of CsDS surfactant in the two different solvents (choline chloride:urea or choline chloride:glycerol). The model test includes the following mathematical models: monodisperse and polydisperse spheres, monodisperse ellipsoids and monodisperse cylinders. The results from the comparison are presented in Fig. S3 and the Chi Square statistic of each fit are listed in Table S1.

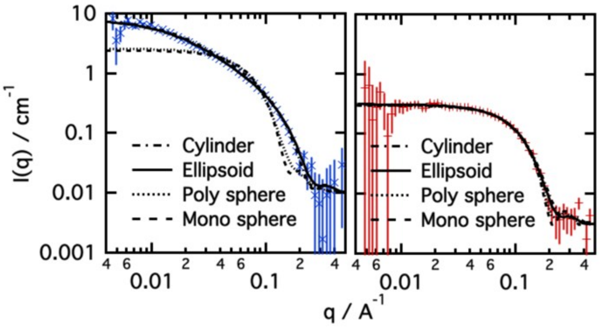

Fig. S3 comparison of best possible fits to CsDS micelles in (a) choline chloride:urea and (b) choline chloride:glycerol using different mathematical models.

Table S1 list of Chi Square statistics corresponding to the models presented in Fig. S2. *This value provides a very low aspect ratio (~ 1.6) and therefore we consider that a cylinder is not the best description of such body.

Model	CsDS in choline chloride:urea	CsDS in choline chloride:glycerol
Monodisperse spheres	142	1.4
Polydisperse spheres	121	1.1
Monodisperse ellipsoids	3.2	0.9
Monodisperse cylinders	2.1	1.0*

The lower the value of the Chi Square statistic, the better the quality of the fit. From the results it can be observed that, in the case of the elongated aggregates, both ellipsoids and cylinders describe the scatterers satisfactorily. Also it was found that the morphology of the scatterers represented by those fits are the same. In the case of globular micelles, both spheres and ellipsoids are suitable options to fit the data. Thus we have selected an ellipsoid model to fit all the data presented here. Such model provides a suitable option to fit all the systems and compare the results obtained. Monodisperse bodies were selected, as this is the most likely scenario considering that micelles are in thermodynamic equilibrium.

SANS results

The Guinier plot was used to determine the radius of gyration (Rg) of the micelles in the dilute regime. This model free approach provides an insight on the size of the aggregates without assuming any particular morphology. The results from the Guinier approach are presented in Fig. S4.

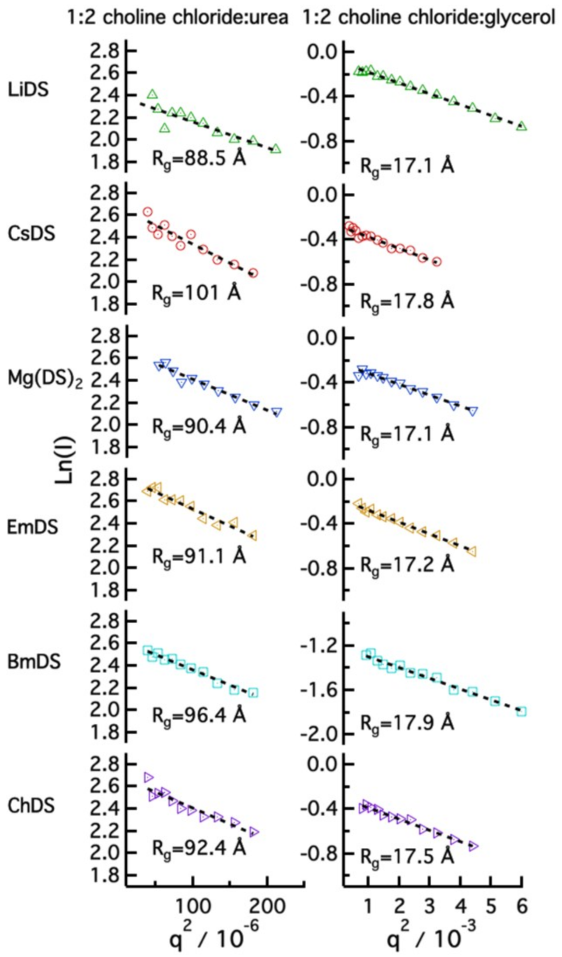

Fig. S4 Guinier approximation and radius of gyration of different micelles in (left) choline chloride:urea and (right) choline chloride:glycerol. The averaged concentration of surfactant corresponds to 39.8±2.5 mM in urea-based DES and 43.3±1.8 mM in glycerol-based DES.

It can be appreciated from these results that changes in the surfactant counterion modifies the size of the aggregates. Further discussion and comparison with model-based fitting is presented in the main text.

Fitting of the highest concentration of surfactants presented here was attempted without accounting for the structure factor. The disagreement is clear from the plot and therefore the implementation of a modified Hard-Sphere structure factor model was needed (See main text for results and description). Here are included the results from both approaches: model with structure factor not included (Table S2) and model with structure factor included (Table S3), both included in Fig. S4.

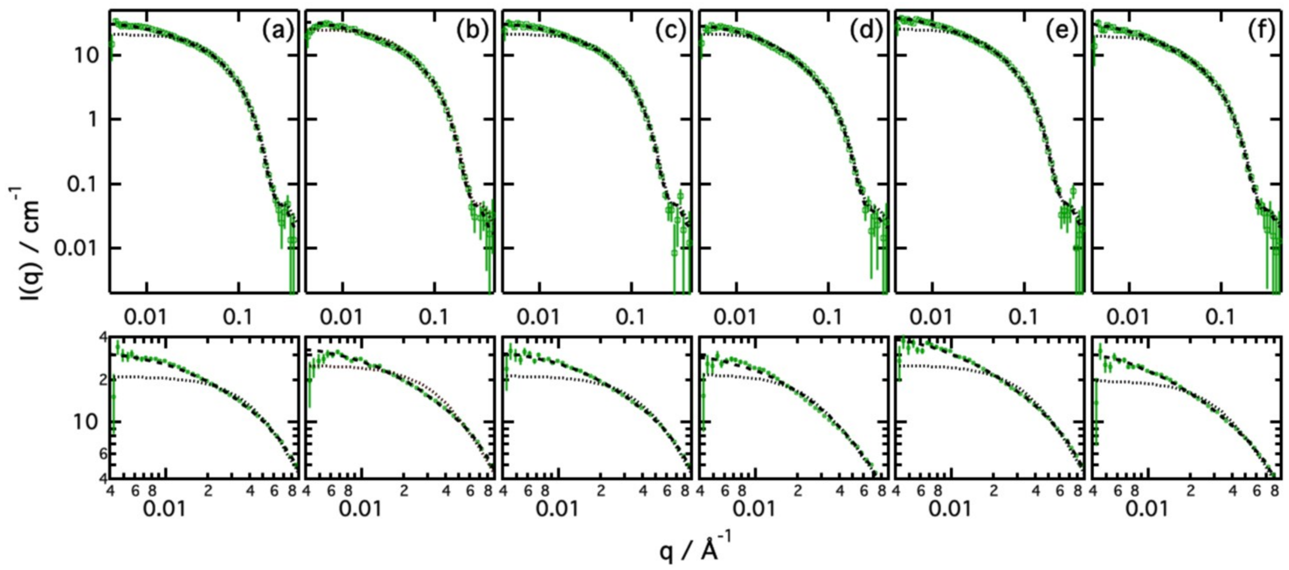

Fig. S4 SANS data and best fits for an averaged concentration of 196±11 mM of (a) h-LiDS, (b) h-CsDS, (c) h-$Mg_{1/2}$DS, (d) h-EmimDS, (e) h-BmimDS and (f) h-ChDS in d-choline chloride:d-urea. Fits using the model that combines form factor and structure factor are represented as black-dashed lines. Black-dotted lines represent the best fits when attempted to fit using the ellipsoid form factor (No S(q) included). The plots below zoom into the low-q region of the data and fits.

Table S2 results from SANS fitting for scattering data from a solution of an averaged concentration of 196±11 mM of different surfactants in choline chloride: urea (best fits with structure factor not included).

Surfactant	r_{eq} / Å	AR	$\phi_{P(q)}$ / 10^{-2}	ϕ_{Calc} / 10^{-2}	R_{eff} / Å	$\phi_{S(q)}$ / 10^{-2}
LiDS	16.5±0.2	4.0±0.2	5.6±0.2	5.6±0.4	-	-
CsDS	16.5±0.3	4.8±0.2	5.5±0.2	5.9±0.5	-	-
$Mg(DS)_2$	16.4±0.2	4.0±0.1	5.3±0.2	5.8±0.3	-	-
EmimDS	16.3±0.3	4.4±0.1	3.3±0.2	3.5±0.2	-	-
BmimDS	16.7±0.2	4.3±0.2	5.4±0.3	6.4±0.7	-	-
ChDS	16.1±0.3	5.3±0.3	4.3±0.2	4.9±0.3	-	-

Table S3 results from SANS fitting for scattering data from a solution of an averaged concentration of 196±11 mM of different surfactants in choline chloride:urea (best fits with structure factor included).

Surfactant	r_{eq} / Å	AR	$\phi_{P(q)}$ / 10^{-2}	ϕ_{Calc} / 10^{-2}	R_{eff} / Å	$\phi_{S(q)}$ / 10^{-2}
LiDS	16.7±0.5	9.6±0.7	5.5±0.2	5.6±0.4	37.2	7.4±0.3
CsDS	17.8±0.4	10.6±0.2	5.4±0.2	5.9±0.5	39.3	7.5±0.6
$Mg(DS)_2$	17.8±0.3	9.3±0.2	5.6±0.2	5.8±0.3	37.5	7.3±0.2
EmimDS	17.6±0.2	10.3±0.4	3.6±0.1	3.5±0.2	38.3	3.7±0.1
BmimDS	18.0±0.4	10.6±0.3	5.4±0.2	6.4±0.7	39.6	6.9±0.2
ChDS	17.5±0.4	12.4±0.8	4.1±0.1	4.9±0.3	40.5	6.4±0.1

The results obtained from both approaches show that ignoring the structure factor contribution to the scattering leads to an under evaluation of the aspect ratio of the micelles of *c.a.* 56 %. Therefore the implementation of the structure factor can lead to a considerably better evaluation of micelle morphology. Following, the plots for all the contrast for the systems are included. Fig. S5 and S6 include those for LiDS, CsDS and $Mg_{1/2}$DS in choline chloride:urea and glycerol, respectively.

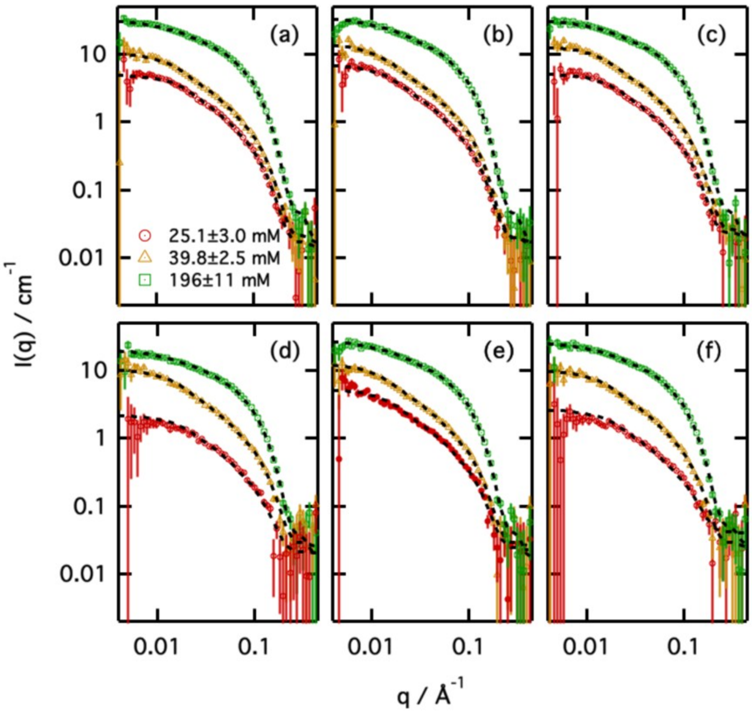

Fig. S5 SANS data and best fits of (a) h-LiDS, (b) h-CsDS and (c) h-$Mg_{1/2}$DS in d-choline chloride:d-urea; and (a) d-LiDS, (b) d-CsDS and (c) d-$Mg_{1/2}$DS in h-choline chloride:h-urea at different surfactant concentration (as quoted in plot a).

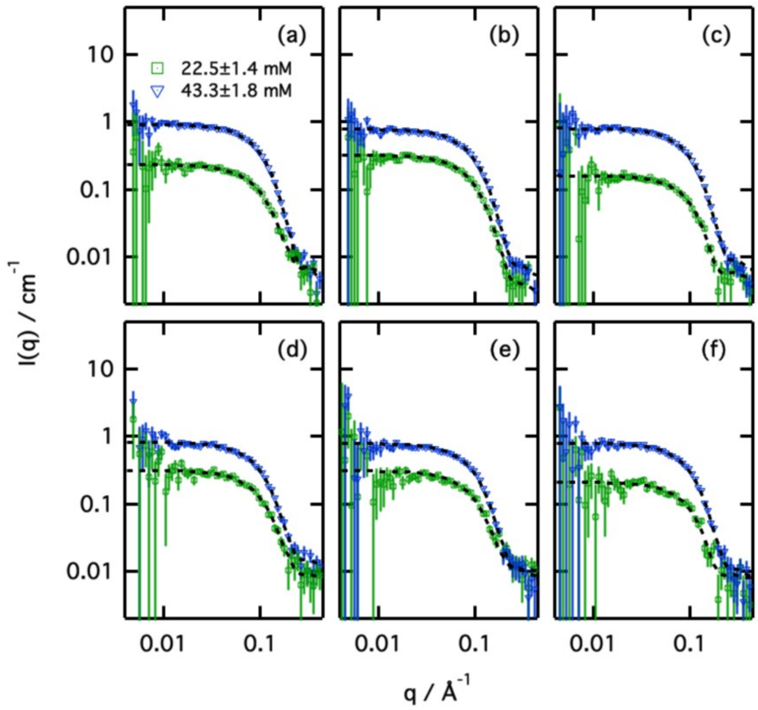

Fig. S6 SANS data and best fits of (a) h-LiDS, (b) h-CsDS and (c) h-Mg$_{1/2}$DS in d-choline chloride:d-glycerol; and (a) d-LiDS, (b) d-CsDS and (c) d-Mg$_{1/2}$DS in h-choline chloride:h-glycerol at different surfactant concentration (as quoted in plot a).

References

1. J. R. Lu, A. Marrocco, T. J. Su, R. K. Thomas and J. Penfold, *J. Colloid Interface Sci.*, 1993, **158**, 303-316.
2. K. Shinoda and T. Hirai, *J. Phys. Chem.*, 1977, **81**, 1842-1845.
3. P. Brown, C. P. Butts, J. Eastoe, D. Fermin, I. Grillo, H.-C. Lee, D. Parker, D. Plana and R. M. Richardson, *Langmuir*, 2012, **28**, 2502-2509.
4. I. Weil, *J. Phys. Chem.*, 1966, **70**, 133-140.
5. T. Arnold, A. J. Jackson, A. Sanchez-Fernandez, D. Magnone, A. E. Terry and K. J. Edler, *Langmuir*, 2015, **31**, 12894-12902.
6. P. H. Elworthy and K. J. Mysels, *J. Colloid Interface Sci.*, 1966, **21**, 331-347.

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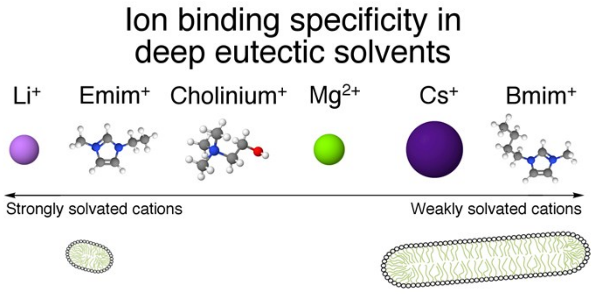

Counterion adsorption unexpectedly changes self-assembly behaviour in deep eutectic solvents.