Experimental report

24/11/2023

Proposal:	**9-12-687**	**Council:**	10/2022

Title: Contrast variation for explaining pD-dependent LCST-alterations in dye-surfactant solutions by locating the dye in dye-surfactant assemblies

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: C12E5 matched samples containing dye and surfactant
Full Contrast Solutions containing dye and surfactant

Instrument	Requested days	Allocated days	From	To
D22	3	2	16/04/2023	18/04/2023

Abstract:

Alkyl ethoxylate surfactants CmEn with m alkyl chain carbon atoms and n ethylene glycol groups are an integral part of industrial and personal consumer products. A common feature of these surfactants in aqueous solution is a lower critical solution temperature (LCST). Addition of a pD-responsive azo dye was observed to increase, decrease or have no effect on the LCST of C12E5 solutions, dependent on solution pD. To explain the mechanism behind this observation, we propose to study the influence of pD, temperature and dye concentration on the morphology of dye-C12E5 micelles with small-angle neutron scattering. Furthermore, we aim to localize the dye within the C12E5 micelles by matching the C12E5 surfactant to the D2O solvent in a contrast variation experiment. This will permit the direct correlation of the dye charge (different states of protonation due to pD changes), its localization within the surfactant micelle and its influence on solution LCST.

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DOI: 10.5291/ILL-DATA.9-12-687

Abstract: The morphology of co-assemblies between the azo dye Blue and the nonionic surfactant $C_{12}E_5$ in an isotonic NaCl solution in D_2O was investigated at a temperature of 10 °C. Morphological changes were observed upon variation of solution pD and correlated with changes in the clouding temperature (CT) of Blue/$C_{12}E_5$ systems. Contrast matching the surfactant $C_{12}E_5$ to the solvent led to the observation of a scattering signal arising from Blue only and permitted the localization of Blue in $C_{12}E_5$ micelles.

Scientific background: Alkyl ethoxylate surfactants C_mE_n with m alkyl chain carbon atoms and n ethylene glycol groups are an integral part of industrial and personal consumer products. A common feature of these surfactants in aqueous solution is a clouding temperature (CT). The behaviour of C_mE_n solutions was intensively studied with scattering techniques and the observed increase in forward scattering intensity upon approaching the CT explained by a combination of micellar growth and attractive interactions between individual C_mE_n micelles.[1,2] Additives may infer with both mechanisms and therefore change the CT of a solution. We investigated the effect of additive polarity on the CT of $C_{12}E_5$ solutions and the morphology of additive/$C_{12}E_5$ co-assemblies without having to consider steric requirements. This was done by changing the polarity of one and the same additive (the azo dye Blue) upon pD variation.

Materials and Methods: The azo dye Blue shows two pK_A values between pD = 0 and pD = 14. At pD = 2 it is present in its acid, neutral form (**BlueH**). It is one-fold deprotonated at pD = 9 (**Blue$^-$**) and two-fold deprotonated at pD = 13 (**Blue^{2-}**). The $C_{12}E_5$ surfactant was used in three different degrees of deuteration: (1) Completely hydrogenated ($hC_{12}hE_5$) (2) Statistical deuteration of the C_{12} alkyl chain with a H:D ratio of 9:91 and a completely hydrogenated E_5 head group ($mC_{12}hE_5$) (3) Statistical deuteration of the C_{12} alkyl chain with a H:D ratio of 9:91 and a completely deuterated E_5 head group ($mC_{12}dE_5$). The last two surfactants were provided by the ESS DEMAX laboratory specifically for the experiment described here. Samples were prepared in an isotonic NaCl solution (I = 154 mM) in D_2O and the pD of each sample adjusted using a 1 M DCl or NaOD solution. Samples were stored at a temperature of 7 °C for a minimum of 24 h before measurement and equilibrated at the measurement temperature of 10 °C for at least 1 h before measurement.

The experiment consisted of three steps: (1) Match point determination step: This served to determine the ratio between $mC_{12}hE_5$ and $mC_{12}dE_5$ at which no form factor scattering is observed. It was successfully determined to $\Phi(mC_{12}hE_5)$: $\Phi(mC_{12}dE_5)$ = 18.1:81.9 (v:v). (2) Recording of "full contrast" SANS curves from samples containing the completely hydrogenated $hC_{12}hE_5$ surfactant and Blue. (3) Recording of $C_{12}E_5$-matched SANS curves from samples containing $mC_{12}hE_5$ and $mC_{12}dE_5$ at the match point and Blue. In all cases, the solvent was prepared with 100 % D_2O.

Experiments were performed on the SANS-instrument D22 with the typical configuration.

Results

Pure $C_{12}E_5$ solutions as a reference: Figure 1A displays experimental SANS curves recorded from $C_{12}E_5$ solutions with different pD. The feasibility of our strategy to change additive polarity, but not the morphology of pure $C_{12}E_5$ micelles upon variation of solution pD is verified by the identity of SANS curves shown in Figure 1A.

pD-dependent morphology of Blue/$C_{12}E_5$ assemblies: Figure 1B displays a representative set of full contrast SANS curves from samples containing the surfactant $hC_{12}hE_5$ and the additive

Blue at variable pD. In contrast to Figure 1A, a pD-dependency of the scattering signal from Blue/$C_{12}E_5$ assemblies is clearly visible and caused by the variation of Blue polarity with variable pD.

Full contrast SANS curves are fitted with the following model:[1]

$$I_q(q) = N \cdot P(q) \cdot S(q) \tag{1}$$

$$C(q) = 1 + \frac{\kappa}{1 + q^2\xi^2} \tag{2}$$

In eq (1), N is the number density of scattering particles and $P(q)$ the single particle form factor, which describes the shape and contrast of a single particle. $S(q)$ is the structure factor, which describes interparticle correlations and could be replaced by the Ornstein-Zernike expression (eq (2)) in case of concentration fluctuations due to attractive interparticle interactions.[1,3] In eq (2), κ is a scaling factor and ξ the correlation length of concentration fluctuations. Form factors for end-capped core-shell cylinders with different core lengths ($20\ \text{Å} \leq L_{\text{core}} \leq 200\ \text{Å}$) and the form factor of a core-shell sphere were systematically applied to fit full contrast SANS curves with eq (1), including Ornstein-Zernike scattering (eq (2)) as $S(q)$. In most cases, best fits were obtained when using the form factor for end-capped core-shell cylinders with $L_{\text{core}} = 40$ Å or $L_{\text{core}} = 66$ Å and eq (2) as $S(q)$. At high pD (≥ 12) and Blue concentration (≥ 6.25 mM), SANS curves were best fitted assuming the form factor of core-shell spheres and a structure factor based on a hard sphere potential.

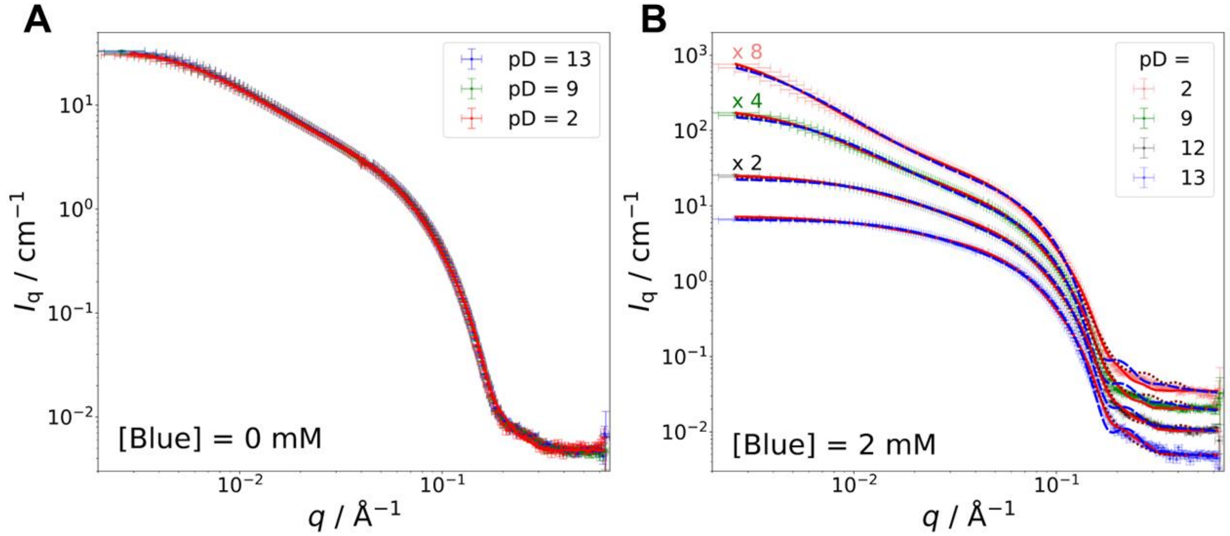

Figure 1: **A** Full contrast SANS curves from solutions containing [$hC_{12}hE_5$] = 25 mM at the indicated pD. An isotonic NaCl solution (I = 154 mM) in D_2O was used as the solvent and SANS curves were recorded at a sample temperature of 10 °C. The red line (___) displays a fit with the form factor model of end-capped core-shell cylinders with a core length of 66 Å including Ornstein-Zernike scattering in place of a structure factor. Experimental SANS curves and the fit overlay. **B** Full contrast SANS curves of solutions containing [$hC_{12}hE_5$] = 25 mM and [Blue] = 2 mM at variable pD. An isotonic NaCl solution (I = 154 mM) in D_2O served as the solvent. SANS curves were recorded at a sample temperature of 10 °C. Red line (___): Fit with the form factor of end-capped core-shell cylinders with a core length of L_{core} = 66 Å and Ornstein-Zernike scattering. Dark red dotted line (….): Fit with the same model, but L_{core} = 40 Å. Blue dashed line (----): Fit with the form factor of core-shell spheres and Ornstein-Zernike scattering.

Upon comparison of fits to full contrast SANS curves it was found, that the Blue/$C_{12}E_5$ assembly size and correlation lengths of concentration fluctuations (ξ) increase with a reduction in the temperature distance (ΔT_{CT}) to the CT. As measurements were performed at the same temperature of 10 °C, variations in ΔT_{CT} were caused by changes to the CT due to a variation in pD and concentration of Blue.

Localization of Blue in Blue/$C_{12}E_5$ co-assemblies: As an example, Figure 2 displays full contrast and $C_{12}E_5$-matched SANS curves from solutions containing Blue and the surfactant at pD = 9. SANS curves from $C_{12}E_5$-matched samples were fitted with almost the same model as SANS curves from full contrast samples, taking into account an additional Guinier contribution due to scattering from individual Blue molecules or small oligomers thereof. As many parameters as possible were fixed to values obtained from the analysis of full contrast SANS curves. In the presented case, this concerns the Ornstein-Zernike parameters κ and ξ as well as the length of core-shell cylinders. Cross section dimensions were fitted and compared to cross section dimensions of Blue/$C_{12}E_5$ co-assemblies that were obtained from fitting full contrast SANS curves. A comparison of core radii and shell thicknesses points towards the localization of Blue^{-} in the palisade- and outer region of $C_{12}E_5$ micelles.

A similar strategy was employed for analysing $C_{12}E_5$ matched SANS curves from samples containing BlueH and $C_{12}E_5$ at pD = 2 and samples containing Blue^{2} and $C_{12}E_5$ at pD = 13. The choice of form- and structure factors was based on results from the analysis of corresponding full contrast SANS curves. The described procedure, which relies on the comparison of cross section dimensions for the full contrast and the $C_{12}E_5$-matched case, permitted the localization of BlueH in the hydrophobic core and the localization of Blue^{2-} in the headgroup region of $C_{12}E_5$ micelles.

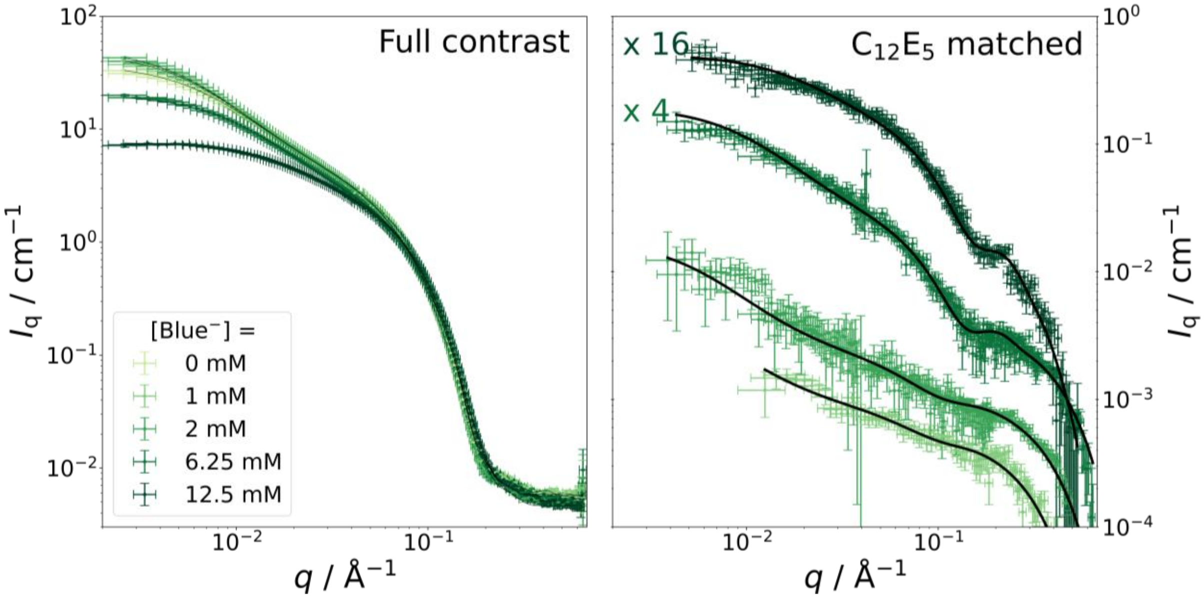

Figure 2: Left: Full contrast SANS curves from solutions containing $[hC_{12}hE_5]$ = 25 mM and Blue^{-} at the indicated concentration at pD = 9. An isotonic solution of NaCl (I = 154 mM) in D_2O served as the solvent and SANS curves were recorded at a sample temperature of 10 °C. Black lines (__) display the best fit with the form factor for end-capped core-shell cylinders and Ornstein Zernike scattering. Right: $C_{12}E_5$ matched SANS curves from solutions containing $[mC_{12}hE_5]+[mC_{12}dE_5]$ = 25 mM at the match point and Blue^{-} at the indicated concentration (same colour code as left image) and pD = 9. Black lines display the best fit with the form factor for "hollow" core-shell cylinders and Ornstein-Zernike scattering, which was added to a Guinier contribution from individual Blue^{-} molecules or small oligomers thereof.

References: [1] Glatter, O. *et al.* Nonionic Micelles near the Critical Point: Micellar Growth and Attractive Interaction. *Langmuir* **16**, 8692–8701 (2000). [2] Cebula, D. J. & Ottewill, R. H. Neutron scattering studies on micelles of dodecylhexaoxyethylene glycol monoether. *Colloid and Polymer Science* **260**, 1118–1120 (1982). [3] Ornstein, L.S. & Zernike, F. Accidental Deviations of Density and Opalescence at the Critical Point of a Single Substance. *Proc. Akad. Sci.* **17**, 793–806 (1914).