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Calix-arene silver nanoparticles interactions with surfactants are charge, size and critical micellar concentration dependent[†]

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The interactions of silver nanoparticles capped by various calix[*n*]arenes bearing sulphonate groups at the *para* and/or phenolic faces with cationic, neutral and anionic surfactants have been studied. Changes in the plasmonic absorption show that only the calix[4]arene derivatives sulphonated at the *para*position interact and then only with cationic surfactants. The interactions follow the CMC values of the surfactants either as simple molecules or mixed micelles.

Micelles are formed by the aggregation of surfactants having a cone like geometry,¹ they are characterised by the critical micellar concentration (CMC), above which no free surfactant molecules go into solution.² The CMCs can be determined by a quite large number of physical measurements of which the surface tension is the most widely used.³ Micelles are used in a vast range of applications varying from soaps and detergents,⁴ through butter or margarine⁵ to the extraction of membrane proteins.⁶ Such applications whereas the former applications are dependent on a subjective feeling by a consumer. It is the field of membrane protein biochemistry that the use of supramolecular surfactants is starting to make an impact.

The calix[*n*]arenes are one of the most widely studied classes of organic host molecules, their biological,⁷ solid-state complexation⁸

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various and assembly properties⁹ have been widely studied. They are known to complex a wide range of organic cations, 10 including alkyl ammonium, 11 and alkylated pyridinium 12 salts. Amphiphilic calix[*n*]arenes have been demonstrated to form various types of assembly in aqueous media. One minor drawback is that calix[*n*]arenes require very considerable modification to introduce reporter groups, with the possible perturbation of the complexation properties. The discovery by Xiong *et al.* that *para-*sulphonato-calix[*n*]arenes can cap silver nanoparticles and that the plasmon resonance bands of the hybrid colloids show strong spectral shifts upon selective interaction with histidine introduces the needed reporter functions. 13 Recently we have shown that the hybrid nanoparticles interact with nucleic bases in a similar manner and that the interactions can lead to aggregation of the colloids. 14 In the present work we report the interactions of three types

In the present work we report the interactions of three types of sulphonato-calix[*n*]arene silver nanoparticles with various cationic, neutral and anionic surfactants. The measured spectral shifts can be used as a novel way to determine CMC values for cationic surfactants. Moreover this behaviour can be used to study the highly non-ideal behaviour of mixed surfactant assemblies.

The chemical structures of the various calix[n] arenes are given in Scheme 1 and those of the surfactants in Scheme 2.



Scheme 1 Structures of the sulphonato calix[n]arenes studied. SC(n)a, SC(n)b and SC(n)c correspond, respectively, to *para*-sulphonato-calix[n]arene, *O*-propyl sulphonate calix[n]arene and *O*-propyl *para*-sulphonato-calix[n]arene; with (n) corresponding to the number of phenolic units in the macrocycle.

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[†] Electronic supplementary information (ESI) available: Full details of the syntheses, along with electrospray mass spectrometry and ¹H NMR spectral details, preparation of the hybrid nanoparticles *via* sodium borohydride reduction, full details of the visible spectrometric characterisation of the formation and stability of the hybrid nanoparticles and the spectrometric titrations. See DOI: 10.1039/ c2cc34670b



Scheme 2 Structures of cationic and neutral surfactants. CPB, CTAB and NOG correspond, respectively, to cetyl pyridium bromide, cetyl trimethyl ammonium bromide and *N*-octyl glucopyranoside.

The calix[n]arenes carrying O-propylsulphonate groups at the phenolic functions were synthesised by treating the parent calix[n]arenes with butyl sultone and a large excess of sodium hydride in tetrahydrofuran as per the method of Shinkai *et al.*^{15,16} The reaction was followed using electrospray mass spectrometry and further additions of the reactants were continued until total substitution was achieved.

Suspensions of nine calix[n]arene capped silver nanoparticles at a concentration of 10^{-3} M were titrated against five surfactants; with CPB and CTAB as cationics; Triton X-100 and NOG as neutral; and SDS as an anioinic.

Of the calix[n]arenes only for SC4a, SC4b and SC4c were there changes in the visible spectra, see ESI[†], with both intensity changes and small changes in maximum wavelength, Fig. 1. The shifts in the plasmon resonance paeks are in accordance with interactions but not aggregation. Thus the presumed cone conformation of these molecules on the surface of the silver nanoparticles is important for complexation.

The work was extended for **SC4a** to cover a range of surfactant concentrations up to ten times the CMC values, shown in Fig. 1. Here there is a clear differentiation between cationic and anionic or neutral surfactants. Measuring the absorbance at 390 nm corresponding to the maximum absorbance in the absence of surfactants or using the maximum absorbance



Fig. 1 Maximum absorbance of *para*-sulphonato-calix[4]arene capped silver nanoparticles (Ag_NP_SC4a) as a function of surfactant concentration. • is CPB; + is CTAB; • is NOG; • is Triton X 100; \blacktriangle is SDS.



Fig. 2 Maximum absorbance of calix[*n*]arene capped silver nanoparticles (Ag_NP_Calix[*n*]arene) as a function of cationic surfactant concentration. (A) With CPB and (B) with CTAB. ♦ is Ag_NP_SC4a;
is Ag_NP_SC4b; ▲ is Ag_NP_SC4c.

shows identical behaviour. Extending further to all calix[4]arene derivatives, for SC4a and SC4c there is a minimum in the absorbance at the CMC value for both CPB and CTAB, Fig. 2. Interestingly with SC4b the behaviour is totally different. Here a decrease in the absorbance to reach a plateau is observed. Such behaviour seems more typical of a molecular interaction independent of the micellisation process. DLS and electron microscopy indicate a lack of aggregation up to surfactant to nanoparticle ratios of 5 : 1, see ESI.[†] However for SC4b the observed DLS values are almost invariant. In the electron microscopy it was observed that at the CMC concentration there is a large degree of variation in the geometry of the objects. Intriguingly for SC4c at 1 : 1 and 5 : 1 ratios, there is formation of small crystallites. Such behaviour might have an impact on nucleation of bio-macromolecules. Thus the presence of the sulphonate group in the para-position is required for CMC dependent interactions.

We have demonstrated how capped nanoparticles can be used as probes for CMC determination in the case of cationic surfactants.

Applications of micellar suspensions often involve the use of mixtures of two or more surfactants, as for example in the extraction of membrane proteins. Here one detergent is used to remove the protein from its lipid bilayer environment and then the first surfactant is stripped away by a stabilising detergent.¹⁷ Obviously while the CMC values of the pure detergents are known, the effects of surfactant protein and how CMC values will change as a function of mole fractions of the various components are non-trivial problems.





Fig. 3 Dependencies of the maximum absorbance of Ag_NP_SC4a mixed with a neutral–cationic surfactant mixture on the molar fraction of Triton X100. (A) With CPB and (B) with CTAB. Inset: Dependencies of the CMC of the cationic surfactant Triton X100 mixture required to reach surface pressure on the molar fraction of Triton X100 in solution. (1) refers to the calculation for the ideal system and (2) denotes experimental data. See ref. 18.

A study by Kharitonova *et al.*¹⁸ on the behaviour of CTAB/ Triton-X100 and CPB/Triton X-100 mixed micelles demonstrated that there was a very strong non-ideal behaviour of the C^{M} (CMC of a mixture). Diminutions of a factor of ten between the ideal behaviour and the experimental values were found. The measurements are quite complicated and time consuming.

In view of this, we used the simple spectroscopic determination of the C^{M} values by using various mole fractions of the mixture in the 96 titre well visible spectrometer. Such measurements require only a few minutes and indeed sample preparation is more time consuming in the experiments. The spectra are given in the ESI⁺, and the variations of the maximum absorbance as a function of the surfactant mole fractions are given in Fig. 3. For comparison the values obtained by Kharitonova are given as insets. It can be clearly seen that values obtained here parallel those previously observed using surface tension isotherms as the analytical tool.

In conclusion we have shown that hybrid silver nanoparticles capped by *para*-sulphonato-calix[4]arene derivatives interact in a critical micellar concentration dependent manner with cationic surfactants. Intensity changes in the plasmon resonance absorption spectral peak intensity can be used to determine the CMC. More importantly the method can be applied directly to the determination of critical micellar concentrations in mixed micellar systems. The method generates a new means of studying critical micellar concentrations in media containing proteins and in particular membrane proteins, work is underway to confirm this application.

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