Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics. This journal is © the Owner Societies 2017

Electronic supplementing information

A novel explanation for the enhanced colloidal stability of silver nanoparticles in

the presence of an oppositely charged surfactant

Sara Skoglund^{a,b*}, Eva Blomberg^{a,c*}, Inger Odnevall Wallinder^a, Isabelle Grillo^d, Jan Skov Pedersen^e and L. Magnus Bergström^{a,f*}

- ^{b.} Present address: Department of Materials and Environmental Chemistry
- Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden
- ^{c.} RISE Research Institutes of Sweden Division Bioscience and Materials, Stockholm, Sweden
- ^{d.}Institut Laue Langevin, DS/LSS, Grenoble, France
- e. Department of Chemistry and Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Aarhus, Denmark
- ^{f.} Present address: Department of Pharmacy, Uppsala University, Uppsala, Sweden

*Corresponding authors: Eva Blomberg (blev@kth.se) Magnus Bergström: (Magnus.Bergstrom@farmaci.uu.se) Sara Skoglund: (sarasko@kth.se)

^{a.} KTH Royal Institute of Technology, School of Chemical Science and Engineering, Surface and Corrosion Science, SE-100 44 Stockholm, Sweden



Figure S1: SANS cross section as a function of the scattering vector q for mixtures of Ag NPs and CTAB (a) or DTAC(b) of varying surfactant concentration.

Least-Square Model Fitting SANS Data Analysis

The intensity in terms of the scattering cross-section per unit mass of surfactant for non-spherical interacting nonspherical micelles can be expressed as follows

$$\frac{d\sigma_m(q)}{d\Omega} = \Delta \rho^2 M P(q) \Big[x_{clust} \Big(1 + \beta(q) \big(S_{att}(q) - 1 \big) \Big) + \big(1 - x_{clust} \big) \big(1 + \beta(q) \big(S_{rep}(q) - 1 \big) \big) \Big]$$
[eq. S1]

M is the molecular mass of a particle and $\Delta \rho$ is the difference in scattering length per unit mass of the solute, between particles with a homogeneous core and solvent. The average excess scattering length density per unit mass of the solute (*i.e.*, scattering length density divided by density of solute) CTAB in D₂O, $\Delta \rho_{CTAB} = -6.66 \times 10^{10}$ cm g⁻¹, was calculated using the appropriate molecular volume $\hat{v}_{CTAB} = 607$ Å³ and the molecular weight $M_{CTAB} = 364.45$ g mol⁻¹.¹.

The micelles are considered to consist of free micelles repelling each other with a double layer force with structure factor S_{rep} coexisting with clusters of micelles attracted by the Ag NPs (invisible in the SANS experiments) with structure factor S_{att} . The fraction of micelles participating in a cluster is denoted x_{clust} whereas the fraction of free micelles equals $1 - x_{clust}$.

P(q) is the orientational averaged form factor which describes the geometrical shape of the micelles². The orientational averaged form factor for triaxial ellipsoidal micelles with half axes *a*, *b* and *c*, related to thickness width and length, respectively, equals³

$$P(q) = \langle F^2(q) \rangle_0 = \frac{2}{\pi} \int_0^{\pi/2} \int_0^{\pi/2} F^2(q, r(a, b, c, \phi, \theta)) \sin \phi d\phi d\theta$$
 [eq. S2]

where

$$F(q, r) = 3[\sin(qr) - qr\cos(qr)]/(qr)^3$$
 [eq. S3]

and

$$r(a,b,c,\phi,\theta) = \sqrt{\left(a^2 \sin^2 \theta + b^2 \cos^2 \theta\right) \sin^2 \phi + c^2 \cos^2 \phi}$$

[eq. S4]

Electrostatic interactions were taken into account using a structure factor $S_{rep}(q)$ as derived by Hayter and Penfold⁴ from the Ornstein-Zernike equation in the rescaled mean spherical approximation.⁵

To account for the cluster formation we have employed a structure factor $S_{att}(q)$ derived for sticky hard spheres of radius r_{HS} outside which an attractive square well pair potential of depth u and width δ is located.⁶ In the original Baxter model the Percus-Yevick closure relation⁷ is used to solve the Ornstein-Zernike integral⁸, which describes the direct and indirect interactions between particles in a solution. It is assumed that the interparticle interaction potential consists of a hard sphere of radius r_{HS} together with a rectangular attractive well pair potential.⁶ The attractive well pair potential is assigned to have a depth u and width δ . An interaction parameter τ , defined as

$$\tau^{1} = 4[\exp(-u/kT) - 1][(1 + \delta/r_{HS})^{3} - 1]$$
[eq. S5]

accounting for the stickiness between the micelles² and thus related to the well potential and volume fraction of surfactant aggregates was also included in the structure factor, as well as the expression for τ defined by Menon *et al.*⁹. This model may be regarded as corresponding to hard spheres with surface adhesion and has previously also been used to describe for example the structure of sterically stabilized silica colloidal particles.^{10, 11}

The structure factors have been included using a so-called decoupling approximation, where $\beta(q) \equiv \langle F(q) \rangle_0^2 / \langle F^2(q) \rangle_0$ [*c.f.* eq. S1].^{12, 13} This approximation assumes that the aggregates are not spherical and will have a small anisotropy and that the interactions between them will not at all be affected by their orientation.

Prior to the fitting of the data, the raw spectra were corrected for background from the solvent, sample cell, and other sources by conventional procedures.¹⁴ Throughout the data analysis corrections were made for instrumental smearing. For each instrumental setting, the ideal model scattering curves were smeared by the appropriate Gaussian resolution function when the model scattering intensity was compared with the measured absolute scale

intensity in least-squares model fitting data analysis. The parameters in the model were optimized by means of conventional least-squares analysis and the quality of the fits was measured in terms of the reduced chi-squared parameter (χ 2) and the errors of the parameters were calculated by conventional methods.^{2, 15} Furthermore we were careful not to introduce any additional fitting parameters unless they give rise to a significantly improved quality of the model fit.



Results from Least-Square Model Fitting Data Analysis

Figure S2: SANS cross section as a function of the scattering vector q for mixtures of Ag NPs and CTAB of varying surfactant concentration (10×CMC (\Box), 5×CMC (\circ), 1×CMC (Δ), 0.8×CMC (∇)) as well as for a solution of Ag NPs only (\circ) and of 2×CMC CTAB only (\Box). Symbols represent SANS data, and the solid lines represent the best fits with a model for micelle clusters in the vicinity of the particles. The curves have been offset for clarification.



Figure S3: SAXS cross section as a function of the scattering vector q for mixtures of Ag NPs and DTAC of varying surfactant concentration (10×CMC (\Box), 1×CMC (Δ), 0.5×CMC (\Diamond), 0.1×CMC (\triangleleft)





and (b) corresponding scattered light intensities after 1 week and 1 month after preparation

Table S1: Results from least square model fit analyses of SANS data for pure surfactant (CTAB (a) and DTAC (b)) micelles as well as samples containing both Ag NPs and surfactant of various concentrations. Pure micelles could be fitted with a model for general ellipsoids with half axes a, b and c given in Ångström units, whereas it was not possible to distinguish the two minor half axes a and b, with the micelle cluster model. For the samples containing both Ag NPs and surfactants v, the interaction parameters τ , the width of the potential δ , and the fraction x_{clust} of micelles forming clusters in close vicinity of the Ag NPs, are shown.

(a)	Pure CTAB	Negatively charged Ag NPs and CTAB				
[CTAB]	2 x CMC	10 x CMC	5 x CMC	1 x CMC	0.8 x CMC	
Fitting	<i>a</i> = 19.9	a = b = 25	<i>a</i> = <i>b</i> = 25	<i>a</i> = <i>b</i> = 25	<i>a</i> = <i>b</i> = 22	
parameters	<i>b</i> = 30.4	<i>c</i> = 57	<i>c</i> = 92	<i>c</i> = 170	<i>c</i> = 205	
	<i>c</i> = 32.6	<i>v</i> = 0.4E-01	v = 0.4E-01	<i>v</i> = 0.40	v = 0.23	
		<i>τ</i> = 0.3Ε-01	<i>τ</i> = 0.3Ε-01	τ = 0.23	τ = 0.18	
		δ = 1.3	δ = 1.3	δ = 0.3	δ = 0.2	
		$x_{clust} = 0.70$	<i>x_{clust}</i> = 0.39	$x_{clust} = 0.79$	$x_{clust} = 0.91$	

(b)	Pure DTAC	Negatively charged Ag NPs and DTAC				
[DTAC]	2 x CMC	10 x CMC	5 x CMC	1 x CMC	0.4 x CMC	
Fitting	<i>a</i> = 10	<i>a</i> = 15	<i>a</i> =10	<i>a</i> = 9	<i>a</i> = 3	
parameters	<i>b</i> = 20	<i>b</i> = 20	<i>b</i> = 24	<i>b</i> = 19	<i>b</i> = 160	
	<i>c</i> = 24	<i>c</i> = 24	<i>c</i> = 24	<i>c</i> = 247	<i>c</i> = 254	
		<i>v</i> = 0.4E-01	<i>v</i> = 0.1E-01	<i>v</i> = 0.9E-02	<i>v</i> = 0.6E-02	
		<i>τ</i> = 0.4Ε-01	<i>τ</i> = 0.1Ε-01	τ = 0. 7Ε-02	τ = 0.6Ε-02	
		δ = 1.5	δ =1.5	δ = 1.4	δ = 0.9	
		<i>x_{clust}</i> = 0.99	<i>x_{clust}</i> = 0.64	<i>x_{clust}</i> = 0.80	<i>x_{clust}</i> = 1.0	

- 1. J. M. Corkill, J. F. Goodman and T. Walker, *Transactions of the Faraday Society*, 1967, **63**, 768-772.
- 2. J. S. Pedersen, *Adv. Colloid Interface Sci.*, 1997, **70**, 171-210.
- 3. P. Mittelbach and G. Porod, *Acta Physica Austriaca*, 1962, **15**, 122-147.
- 4. J. B. Hayter and J. Penfold, *Molecular Physics*, 1981, **42**, 109-118.
- 5. J.-P. Hansen and J. B. Hayter, *Molecular Physics*, 1982, **46**, 651-656.
- 6. R. J. Baxter, *The Journal of Chemical Physics*, 1968, **49**, 2770-2774.
- 7. J. K. Percus and G. J. Yevick, *Physical Review*, 1958, **110**, 1.
- 8. L. Ornstein and F. Zernike, *Zeitschrift für Physik A Hadrons and Nuclei*, 1918, **19**, 134-137.
- 9. S. Menon, C. Manohar and K. S. Rao, *The Journal of chemical physics*, 1991, **95**, 9186-9190.
- 10. M. Duits, R. May, A. Vrij and C. G. De Kruif, *The Journal of Chemical Physics*, 1991, **94**, 4521-4531.
- 11. C. G. De Kruif and J. C. Van Miltenburg, *The Journal of Chemical Physics*, 1990, **93**, 6865-6869.
- 12. M. Kotlarchyk and S. H. Chen, *Journal of Chemical Physics*, 1983, **79**, 2461-2469.
- 13. J. B. Hayter and J. Penfold, *Colloid and Polymer Science*, 1983, **261**, 1027-1030.
- 14. J. P. Cotton, in *Neutron, x-ray and light scattering: introduction to an investigative tool for colloidal and polymeric systems*, eds. P. Lindner and T. Zemb, North-Holland, Amsterdam, 1991, p. 19–31.
- 15. P. R. Bevington and D. K. Robinson, *McGraw–Hill, New York*, 2003.