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Supporting Information to

Interactions between Large Colloids and Surfactants

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Electrokinetic techniques are certainly very powerful tools to characterize the electrical state of the particles in suspensions. In particular, electrophoresis is perhaps the most useful (as long as the particle concentration is low) and surely one of the best studied methods.

The increase in the electrophoretic mobility from -4.1 to -5.6 (in practical units), when 5 mM SDS is added, in the absence of $C_{12}E_5$ is a clear proof of SDS adsorption. In addition, we performed mobility determinations as a function of SDS concentration. The data, shown below, confirm our explanations based on SDS adsorption. In the absence of any structural changes in the interface an increase of the mobility is associated to an increase of the particle charge. One can estimate the value of this increment of charge as follows: if a bare silica particle has an electrophoretic mobility value of -4.1×10^{-8} $m^2V^{-1}s^{-1}$ (as determined in the paper), then using a complete and contrastable theory that involves numerical calculation [S. Ahualli, A.V. Delgado. S. Miklavcik, L.R. White, *Langmuir* **22** (2006) 7041-7051] we obtain a charge Q_{bare} = - 2.40x10^{-15} C. For the particles in contact with SDS, the predicted charge is $Q_{(bare + SDS)}$ = - 1.14x10^{-14} C. Then the number of molecule in excess of SDS associated to this difference of charge, under the consideration of one elementary charge per molecule, is approximately 56250 molecules. For a spherical particle with 250 nm radius, this corresponds to 0.12 μmol/m^2 (or ~ 14 nm^2/molecule, corresponding to a mean distance of ~3.7 nm between adsorbed molecules). This value is much lower than that obtained by Thibaut et al. [*Langmuir*, **16** (2000) 9192-9198] for the maximum non-ionic surfactant adsorption (5.3

μmol/m^2). It is hence possible that the relatively small amount of SDS adsorbed went unobservable in those experiments.

Please note that our aim is not to quantify the number of molecules adsorbed; we rather focussed on the information that can be obtained from electrokinetics concerning the surfactant association (in bulk or on the particle) in dependence of the mixing sequence. Of course, we cannot quantify the adsorbed amount of the non-ionic surfactant by means of electrophoresis However, we can answer questions like that proposed by Thibaut et al. at the end of the conclusion in their paper: "*even if the non-ionic surfactant adsorbed amount decreases with SDS concentration it cannot be excluded that the remainder layer is a mixture of both anionic and non-ionic surfactants*". That is, our results are not contradictory to theirs, we are probably sweeping a different concentration range.

We call "supercharge" in the sense that charge of the same sign is adsorbed on the particles. In the paper of Penfold et al. [*Langmuir*, **18** (2002) 5755-5760] it was mentioned: "*For the negatively charged surface silica surface, SDS alone would not adsorb*…". In this sense, we consider this effect as" unexpected". Even more, if we add $C_{12}E_5$ in a second step, we obtain a very high value of mobilities that the classical electrokinetic theory [R.W. O'Brien, L.R. White, *J. Chem. Soc. Faraday Trans.* 2, **74** (1978) 1607-1626] cannot explain. We propose the explanation that an adsorbed layer of mixed surfactants coats the particles, thus increasing the mobility.

Our explanation for the influence of the non-ionic surfactant is not that an increase of the radius causes a decrease in the mobility. It is known [Lyklema, J. in *Fundamental of Interface and Colloid Science*; Vol II: Solid-Liquid Interfaces. Chapter IV. Electrokinetics and Related Phenomena, Academic Press, San Diego, 1995] that the electrophoretic mobility is given by the zeta potential that is, the electric potential at the limit of the stagnant layer or slip plane. If this layer is shifted outwards, due for example to the adsorbed micelle layer, the electric potential suffers a strong variation as it can be seen in figure SI_1 below.

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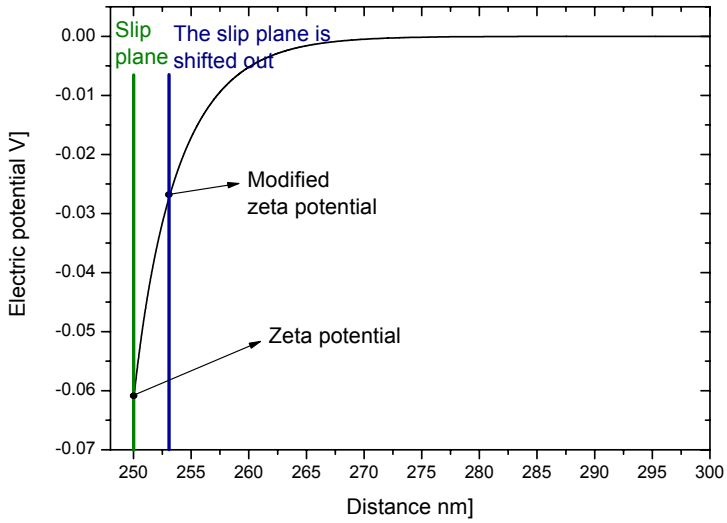

Figure SI_1: This figure represents the electric potential as a function of the distance to the particle center. This distribution was calculated by means of a numerical calculation [*Langmuir* **22** (2006) 7041-7051] around a silica particle with the same size as the silica used in the paper and a charge of 1×10^{-14} C. Hence, if the slip plane is shifted out by just a few nanometers due to the presence of one, more or less dense, layer of nonionic micelles, the zeta potential will essentially decrease and so will the electrophoretic mobility.

Mobility measurement as a function of SDS concentration

In a new series of experiments the values of mobility were measured as a function of SDS concentration and used to fit the charge of the particles:

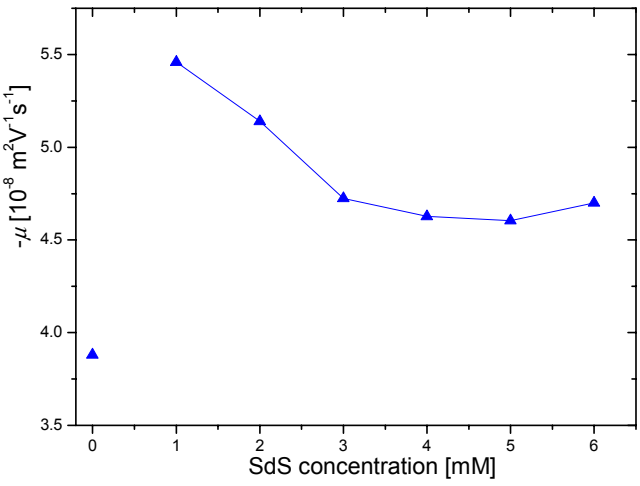

Fig. SI_2: Experimental mobility as a function of SDS concentration

The fitted zeta potential from these data has a similar decreasing trend:

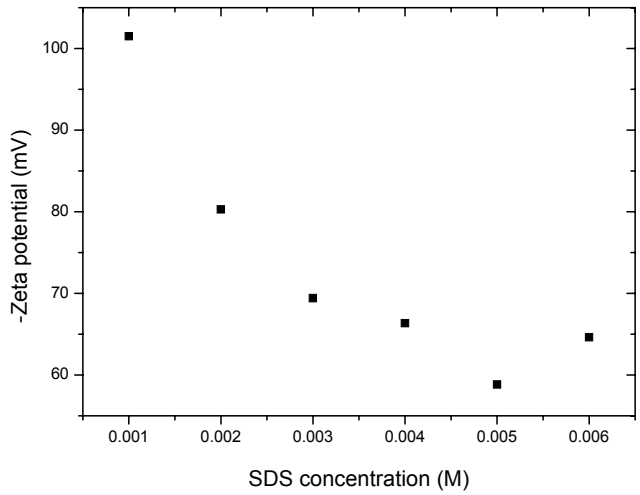

Fig. SI_3: Fitted zeta potential from the mobility data as a function of SDS concentration

The decrease in the mobility and zeta potential with SDS concentration is the behaviour expected when ions, not interacting specifically with the surface (indifferent ions), are added to the solution.

We can understand this behaviour in the following way: the particle and its double layer as a whole can be modelled as a capacitor, in such a way that if an increasing ionic concentration causes a thinner double layer (a larger capacitance). Then, at constant charge, the potential between the plates decreases. So, even at constant charge, we can expect a reduction of the mobility with ion concentration as we show in the following theoretical calculation for the mobility of plain silica at different sodium concentrations (Fig. SI_4).

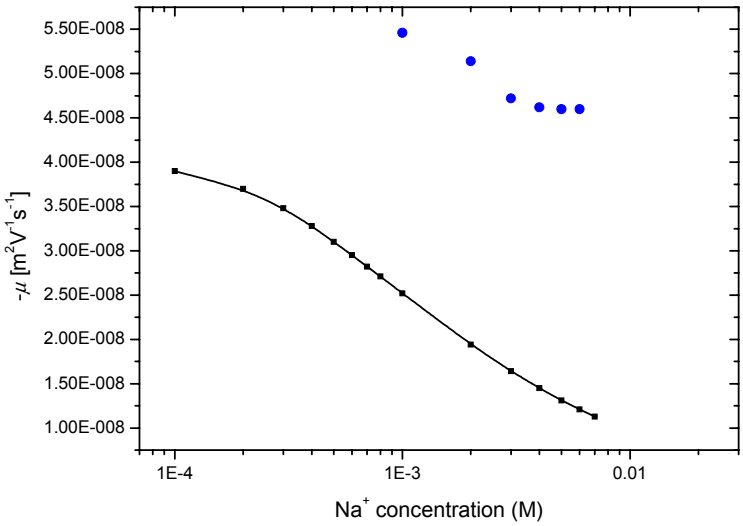

Fig. SI_4: Theoretical mobility as a function of ion concentration at a fixed charge of the particle. The experimental data (●) are also represented for comparison.

Even more, a mobility reduction is compatible with an increase in the charge! In order to prove this, we have fitted the charge of the particles with and without SDS from the experimental values of the electrophoretic mobility, and we obtain the following result (Fig. SI_5):

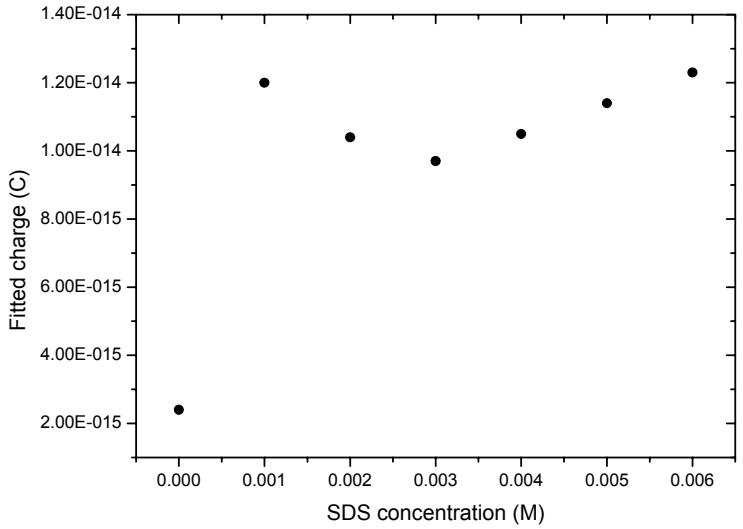

Fig. SI_5: Fitted values of the particle charge from the experimental value of mobility (Fig. SI_2), as a function of SDS concentration.

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We can observe how, at the beginning, the trend is dominated by the double layer compression influence, but when the concentration of SDS is higher, the charge clearly increases. This can only be explained by admitting the adsorption of SDS. This is also confirmed by the observation that, in the whole range of SDS concentration, the charge of the silica+SDS systems is clearly higher than that of plain silica.