Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

The influence of negatively charged silica nanoparticles on the surface properties of anionic surfactants: electrostatic repulsion or the effect of ionic strength?

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Supporting Information

Figure S1 shows the surface tension isotherms for two systems with defined KNO_3 and KOH concentration. In S1.a, the salinity and the pH are high enough to assume that the ionic strength of the system does not change considerably by addition of surfactant. The data reported in Figure S1.a shows that the addition of nanoparticles has no influence on the surface behavior of the system. This could be the result of the screening effect of ions leading to zero repulsive forces, or the fact that the addition of silica nanoparticles does not change the surface properties of the SDBS solution as the ionic strength of the system is constant. On the other hand, a small difference in the curves with/without Np is evident at 2 mM KNO_3 concentration (see Figure S1.b). However, as the increase in ionic strength of the system is more that 50% due to change in concentration of surfactant one cannot completely link this to the electrostatic forces.

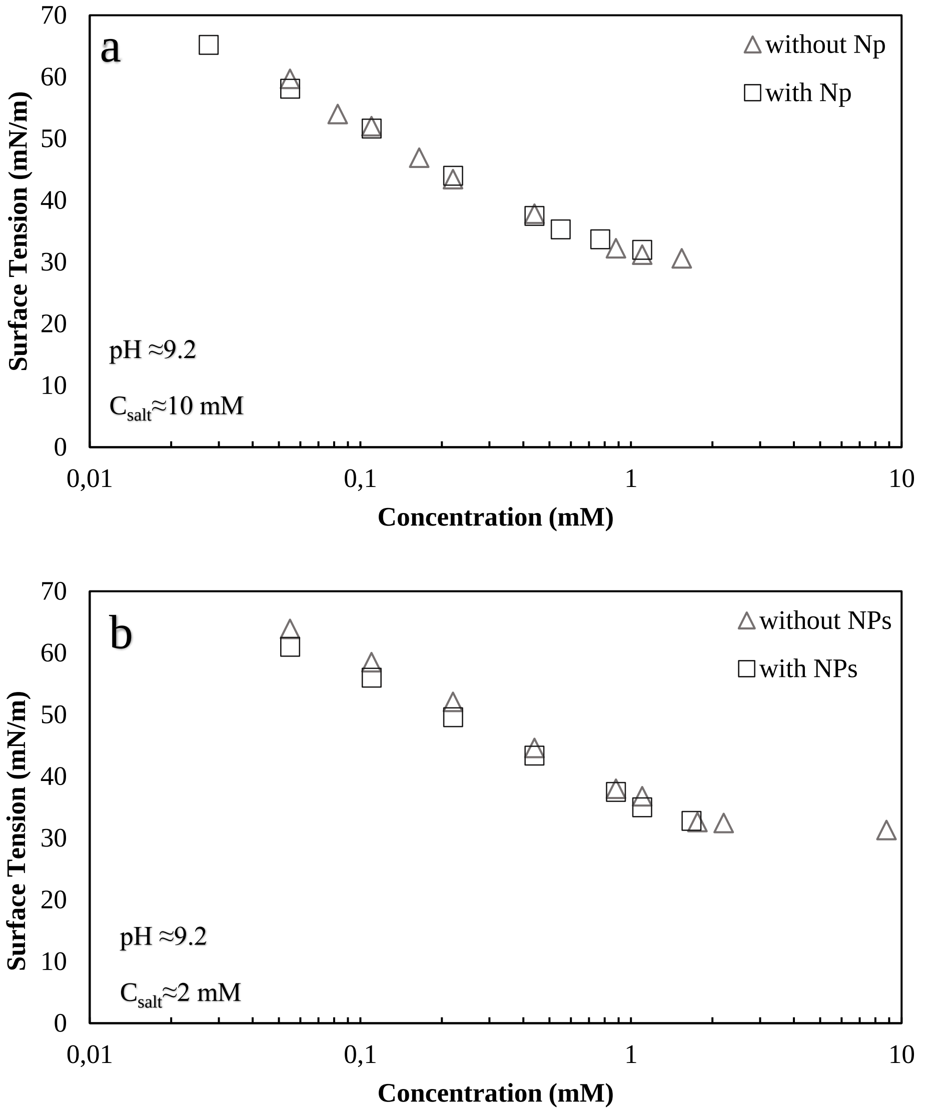

Fig. S1. The effect of 1wt% of Levasil 50/50 on the equilibrium surface tension of SDBS solutions at fixed pH and salinity. a) pH=9.2 and 10 mM KNO_3, b) pH=9.2 and 2 mM KNO_3

Figure S2 shows the dynamic behavior of 0.11 mM SDBS solutions at different KNO_3 concentrations. The results reported in Figure 6b are the end points of this figure.

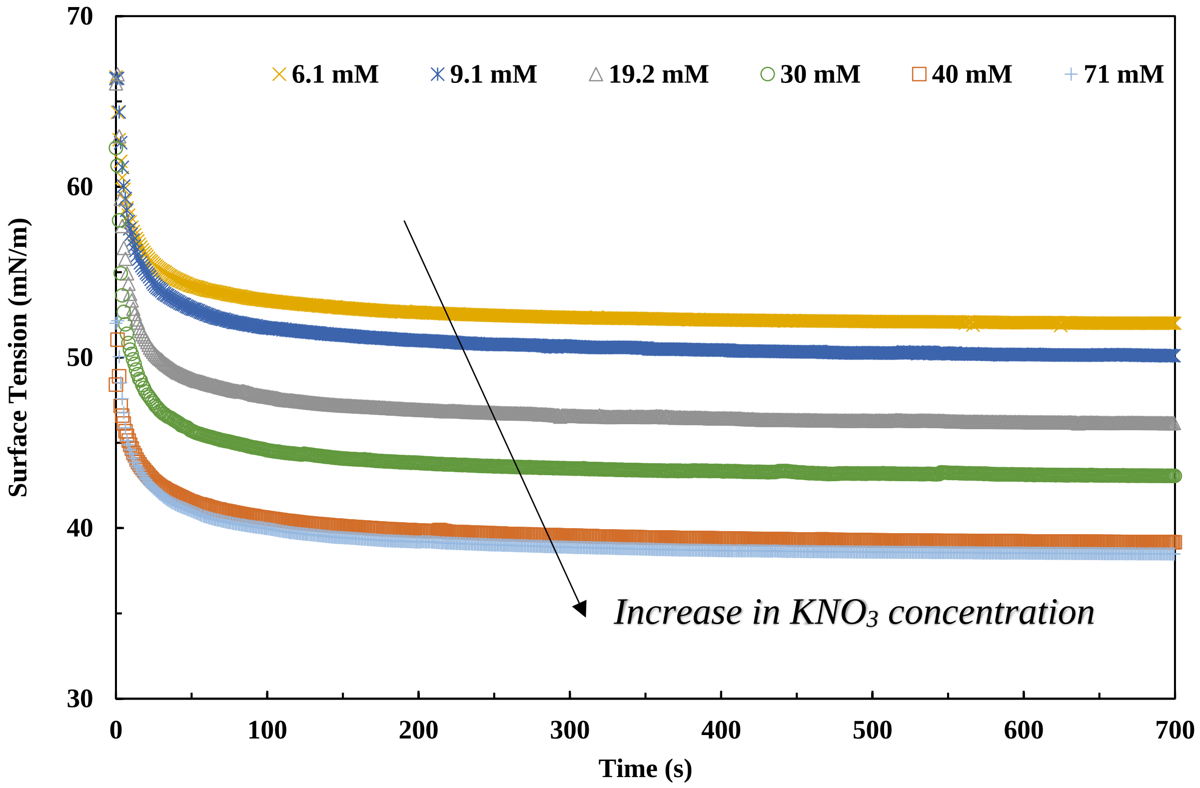

Fig. S2. The effect of KNO_3 concentration on dynamic surface tension of 0.11 mM SDBS solutions. For better visualization the error bars are not indicated; however, all measurements are repeated at least 3 times.

The formation of micelles was investigated by measuring the conductivity of the aqueous solution. Figure S3 plots the conductivity as a function of SDBS concentration. In the main manuscript, we employ the CMC value obtained by conductometry to obtain the surface tension of the pure surfactant.

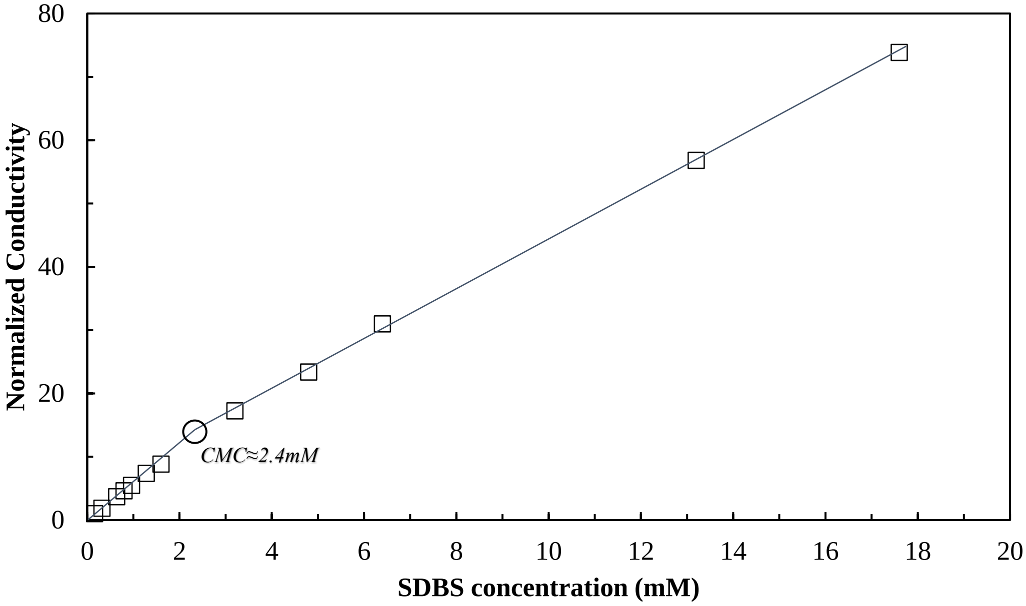

Fig. S3. Conductivity of aqueous solutions as a function of SDBS concentration. The conductivity values are normalized to that of a 0.22 mM SDBS solution, which corresponds to the lowest measured concentration in this experiment.

In the following, we give details on our concept of the “permitted” liquid volume. First, it is necessary to check whether the assumption of isolated particles is valid. For this purpose, we calculated the mean distance between the particles assuming a homogeneous particle distribution and compared it to length scale that potential reduces to zero. For concentrations as low as 0.1 CMC the assumption holds true. Then we considered r^* as the distance in which the electrostatic potential reaches following criterion

$$\left(\left| \psi = \psi_0 \frac{R_p}{r} e^{-\kappa(r-R_p)} \right| < 2.5mV \right)$$

We can calculate the permitted liquid volume according to

$$V_{free} \approx V_{total} - N_{NPs} \times \frac{4}{3}\pi r^{*3}$$

Where N_{Np} is the number of particles within system determined by the weight fraction and the particle size.

Hence, the equivalent concentration of the surfactant can be determined by:

$$C_{eq} = \frac{C_{initial} \times V_{total}}{V_{free}}$$

where C_{initial} is the initial concentration of the surfactant in mM and V_{total} is total volume of the solution. The normalized concentration of the surfactant can further be defined by

$$\bar{C}_{eq} = \frac{V_{total}}{V_{free}} = \frac{V_{total}}{V_{total} - N_{NPs} \times \frac{4}{3}\pi r^{*3}}$$

As already mentioned in the main article text, there are discrepancies in the literature regarding the effect of nanoparticles on the surface tension of surfactant solutions. Some of them are addressed in our article. However, the effect of the nanoparticle mass fraction on the equivalent concentration of the anionic surfactant is not very clear. The equivalent concentration of surfactant was introduced by Vatanparast et al [1] as the concentration of a pure surfactant solution that has the same equilibrium surface tension as the surfactant solution with nanoparticles. For example, 0.1 CMC of SDS in presence of 1 wt% Np 9 nm has an equal ST to 0.2 CMC pure SDS solution [1]. Figure S4 presents the results of two different studies on the effect of silica nanoparticles on the surface behavior of SDS molecules. As it is evident from this figures, it is not clear whether the equivalent concentration of surfactant is an injective function of the Np mass fraction. We believe that multiple factors such as the surfactant CMC value, the pH, the actual ionic strength (considering dissociation and additional solutes introduced by the Np dispersion medium) have to be considered along with possible electrostatic repulsion effects.

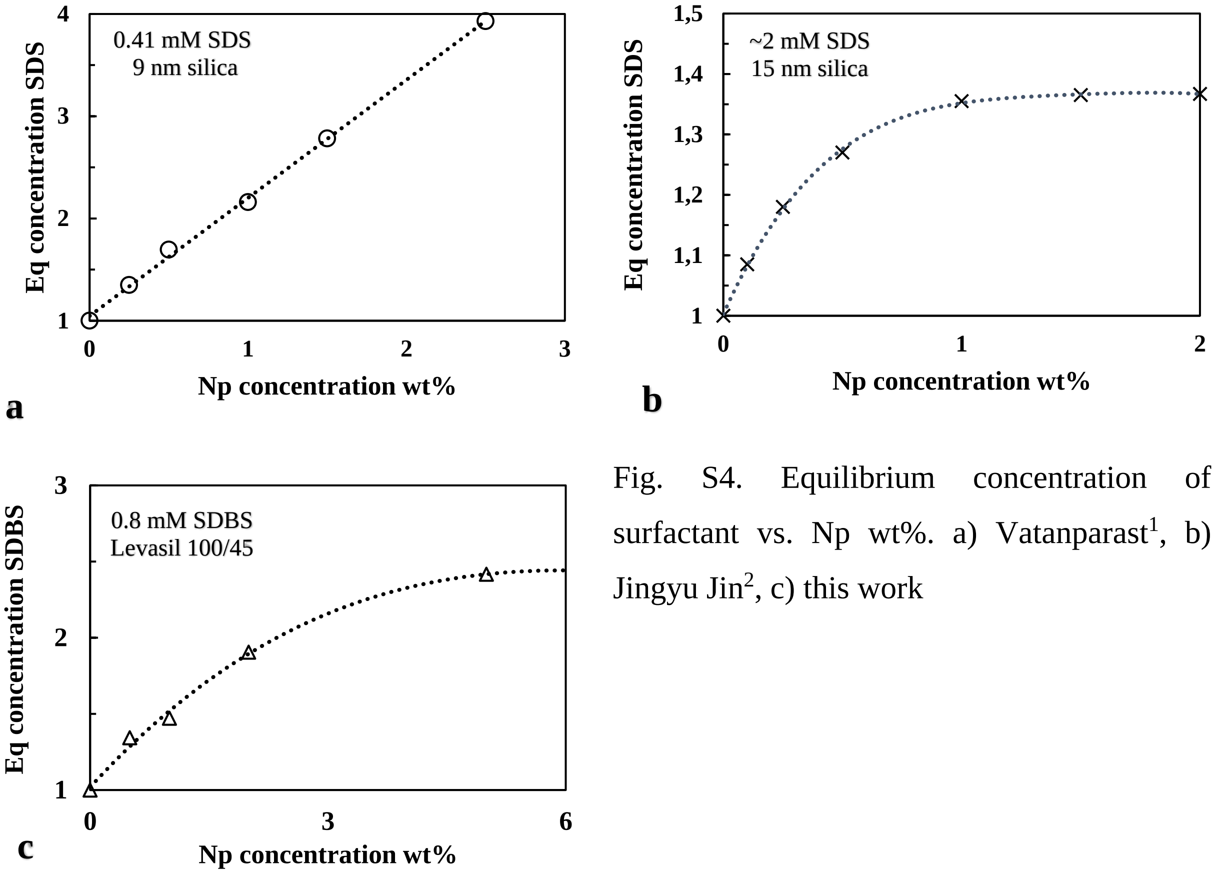

Fig. S4. Equilibrium concentration of surfactant vs. Np wt%. a) Vatanparast[1], b) Jingyu Jin[2], c) this work

REFERENCES

1. Vatanparast H, Samiee A, Bahramian A, Javadi A. Surface behavior of hydrophilic silica nanoparticle-SDS surfactant solutions: I. Effect of nanoparticle concentration on foamability and foam stability. *Colloids Surfaces A Physicochem Eng Asp*. 2017;513(December 2016):430-441. doi:10.1016/j.colsurfa.2016.11.012

2. Jin J, Li X, Geng J, Jing D. Insights into the complex interaction between hydrophilic nanoparticles and ionic surfactants at the liquid/air interface. *Phys Chem Chem Phys*. 2018;20(22):15223-15235. doi:10.1039/c8cp01838c