# Supplementary Materials

According to the classical Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory, increased salinity triggers the coagulation of lyophobic colloidal systems. During aggregation, the turbidity of the system increases when the average size of the scattering particles enlarges. Therefore, a simple spectrophotometer working with a visible wavelength is able to detect and analyze the aggregation kinetics of many colloidal systems. We set a 570 nm wavelength by using a Beckman DU 7400 spectrophotometer, and the absorbance was recorded for 120 s in each experiment. The scattering cell was rectangular with a 1 cm path length. Equal volumes (0.3 mL) of salt and particle solutions were mixed and injected into the cell. The following Figure 1 shows a typical aggregation experiment of a colloidal system partially hydrophilic.

Figure 1. Variation of the optical absorbance (λ = 570 nm) with time for a hydrophilic colloidal system at different NaCl concentrations: 0.003 M (blue inverted triangles ▼), 0.005 M (green right-pointing arrowheads ▶), 0.008 M (orange left-pointing arrowheads ◀), 0.013 M (white squares □), 0.02 M (cyan diamonds ◆), 0.04 M (red squares ■), 0.055 M (pink stars ★), 0.09 M (dark triangle ▲), 0.13 M (grey circle ●), and 0.5 M (yellow pentagons ⬠). The black straight lines represent the initial slopes (dAbs/dt), that are necessary to calculate the Fuchs factor "W".
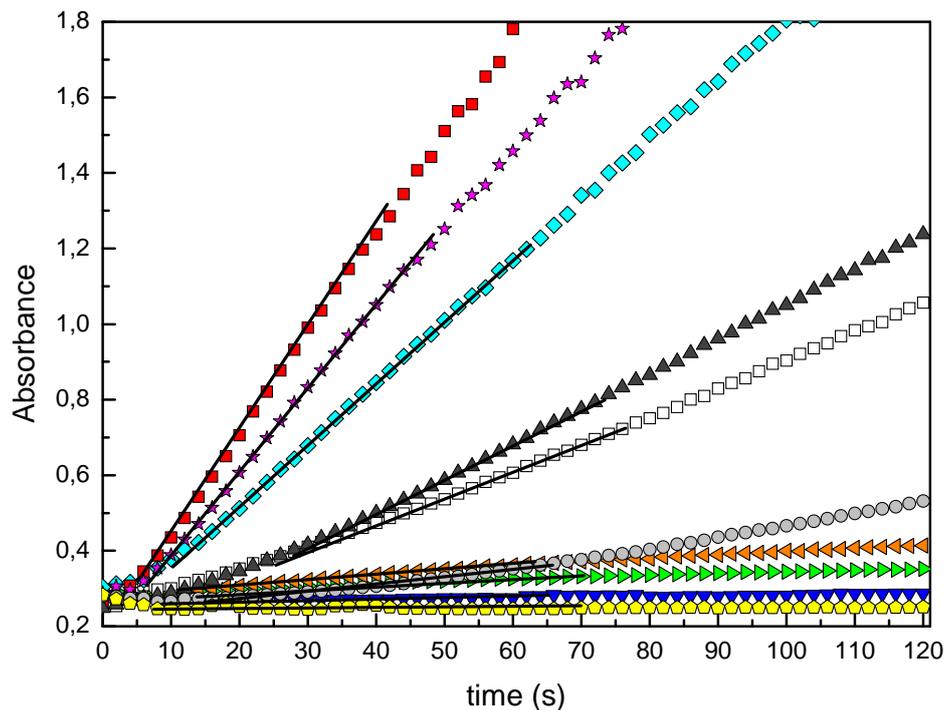
As can be seen, an increment of the salt concentration speeds up the aggregation kinetics, as predicted by the DLVO theory. However, in hydrophilic systems, the kinetics may slow down if the salinity is increased even more. This "anomalous" behaviour is not explained by the DLVO theory, and the origin of this phenomenon must be sought in the repulsive hydration forces. Information on the kinetics-aggregation constant "*k*" of dimmer formation can be derived from these curves. The initial slopes of the *absorbance vs. time* curves (dAbs/dt) can be directly related to *k* by [1]:

$$\frac{dAbs}{dt} = \frac{(C_2/2 - C_1)N_0^2 l}{2.3}k \tag{1}$$

where C_1 and C_2 are the scattering cross-sections of a monomer and a dimmer, respectively, N_0 is the initial particle concentration, and l is the optical path through the cuvette. Nevertheless, stability is usually evaluated by calculating the Fuchs factor (W), instead of calculating the k values by using Equation 1. As mentioned in the main text, the Fuchs factor (also called "stability factor") is related to the number of collisions that must suffer two colliding particles before they keep definitively stuck [2]. Therefore, when $W = 1$ the system is completely unstable, while $W = \infty$ indicates total stability. It is easy to calculate the Fuchs factor at every salt concentration from the curves shown in Figure 1 by using the following equation:

$$W = \frac{k_f}{k_s} = \frac{(dAbs/dt)_f}{(dAbs/dt)_s} \tag{2}$$

where "k_f" refers to the fastest aggregation-kinetics constant, and the subscript "s" refers to slower coagulation rates. This is shown in Figure 2, where the dependence of W on the salt concentration has been plotted.

Figure 2. From those experimental data shown in Figure 1, one can derive the Fuchs factor "W" as a function of salt concentration. The dashed line serves to guide the eye for locating the CCC value, while the dotted line is for the CSC.
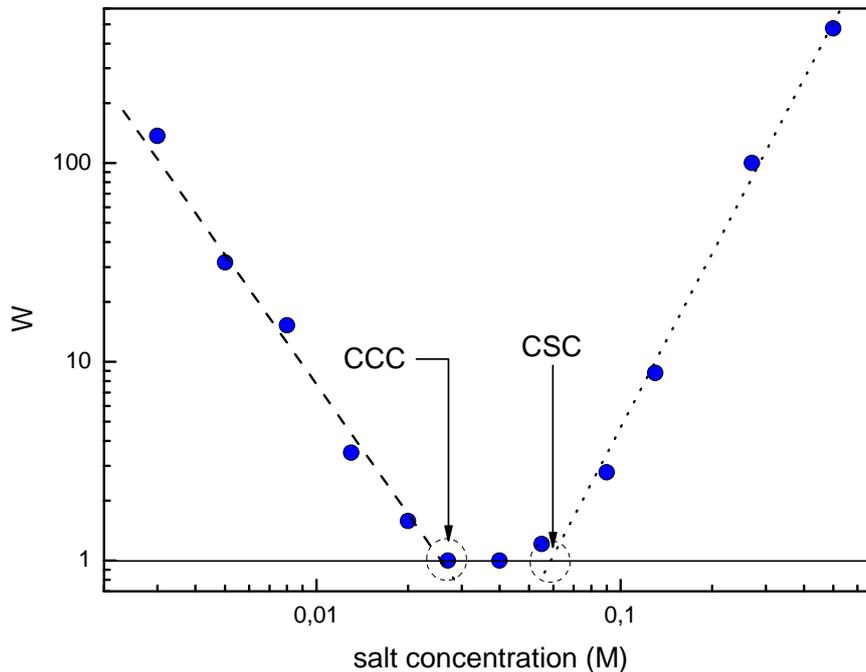
The double-logarithmic scale becomes very useful to estimate the critical coagulation concentration (CCC) and the critical stabilization concentration (CSC), which are fundamental parameters in colloidal-stability studies. The CCC value is the minimum salt concentration needed to make the interaction energy barrier acting between the surface of two colliding particle vanish. It is related to destabilization processes and it indirectly gives information on the surface-charge density of the particles; a low CCC means low stability caused by a low surface-charge density. However, the CSC value—defined as the minimum salt concentration at which the system begins to re-stabilize when

salinity is increased even more because the energetic barriers grows again—is associated with the surface hydrophilicity. This kind of restabilization phenomenon at high salt concentrations is well known in hydrophilic colloidal systems and is governed by hydration forces [3, 4, 5]. Briefly, the microscopic origin of these forces must be sought in the local order of water and hydrated ions located near any hydrophilic surface. The hydration of the surface and ions reduces the free energy of the system. An overlap of the ordered-solvent layers near two mutually approaching surfaces creates a repulsive structural force. Before two particles can collapse, a partial dehydration of the surface polar groups and the ions located near the interface must occur, which leads to an increase in the system energy, resulting in a repulsive force that avoids particle contact and prevents the coagulation of the system. Since this force is dependent on the local concentration of hydrated ions, the repulsive interaction among two colliding particles increases with salinity. This is the explanation of the fact that an instable system at low or moderate ion strength may become stable when the salt concentration increases to high values. It should be noted that CSC values increase when the hydrophilicity decreases; hence a low CSC value means high hydrophilicity. Therefore, there are two important aggregation parameters that give information about two surface characteristics.

The interested reader can be found elsewhere [6] the expressions supplied by the DLVO theory (and its extension to consider the hydration forces) that relate the CCC and CSC values to surface electric potentials and hydrophilic characteristics, respectively, of the particle surface.

References

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