Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary information

For

Unification of Lower and Upper Critical Solution Temperature Phase Behavior of Globular Protein Solutions in the Presence of Multivalent Cations

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Video S1: Phase separation of the BLG-YCl_3 samples with c_p of 40 mg/ml, c_s of 4 mM (right sample), and 10 mM (left sample) in a cold water bath (left beaker) and in a hot water bath (right beaker) with 4X playback speed.

Video S2_LCST: Microscopic video collected during LCST phase transition of the BLG-YCl_3 solution with c_p of 40 mg/ml and c_s of 4 mM. The total real time of the video is 150 sec.

Video S3_UCST: Microscopic video collected during UCST phase transition of the BLG-YCl_3 solution with c_p of 40 mg/ml and c_s of 10 mM. The total real time of the video is 360 sec.

SAXS data analysis to quantify the interaction: We have fitted the SAXS data using a sticky hard sphere (SHS) model with an ellipsoidal form factor. The interaction potential between the particles is given by [1,2]

$$\beta U(r) = \begin{cases} \infty & r < \sigma = 2R \\ -\beta u_0 = \ln\left(\frac{12\tau\Delta}{\sigma+\Delta}\right) & \sigma < r < \sigma + \Delta \\ 0 & r > \sigma + \Delta \end{cases} \qquad \text{------------ (1)}$$

where *R* is the particle radius, τ is the stickiness parameter, Δ is the width of the square well and $\beta = 1/k_BT$. In the limit of $\Delta \rightarrow 0$, the reduced second virial coefficient $\frac{B_2}{B_2^{HS}}$ is given by

$$\lim_{\Delta\to 0} \frac{B_2}{B_2^{HS}} = 1 - \frac{1}{4\tau} \qquad \text{----------- (2)}$$

where B_2^{HS} is the second virial coefficient of a hard sphere. Here, positive B_2 values correspond to repulsive interactions and negative B_2 values correspond to attractive interactions. Typical fits of the SAXS data to the above model are shown in Fig. S1.

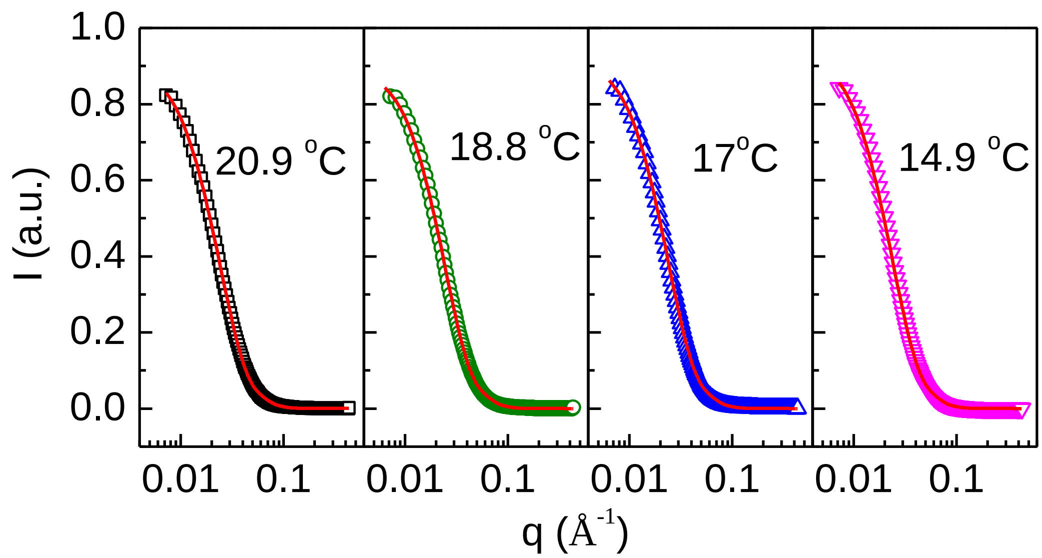

Figure S1: Typical fits (red solid lines) to the SAXS data (symbols) of the BLG-YCl_3 sample with c_p = 6.6 mg/ml and c_s = 2.5 mM (UCST type) at different temperatures as indicated by the legends in the respective panels.

In this model, it is important to note that, the stickiness parameter, τ (related to the second virial coefficient) is mutually dependent on the dimension of the particle, *R* [1,2]. Therefore, in the current analysis, we used an ellipsoidal form factor (reflecting clusters of protein molecules) with the two axis lengths fixed at 41 Å and 86Å [3,4] and obtained the interaction parameter, B_2/B_2^{HS} for the sample BLG-YCl_3 with c_p = 6.6 mg/ml and c_s = 2.5 mM exhibiting UCST behavior (Fig. 3 of the main manuscript) which is shown in Fig. S2.

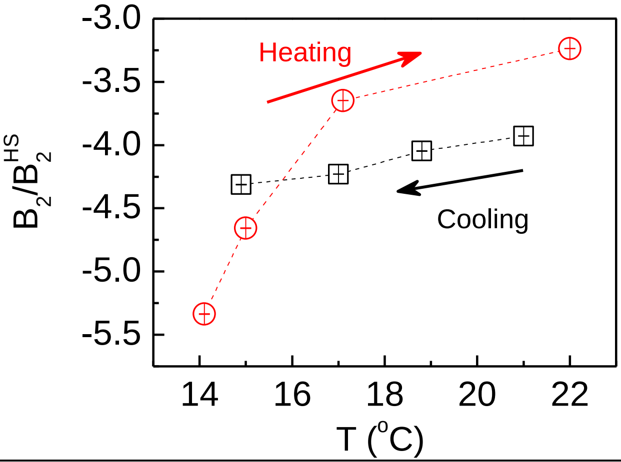

Figure S2: Reduced second virial coefficient as a function of temperature obtained from the SHS model fit to the SAXS profiles of BLG-YCl_3 samples with c_p = 6.6 mg/ml and c_s = 2.5 mM showing an increase in the values of B_2 with decreasing temperature. Error bars are smaller than the symbols.

Fig. S2 indicates that the strength of the attraction (values of B_2/B_2^{HS}) increases with decreasing temperature which could be responsible for the UCST behavior. The enhanced reduction in the case of heating could possibly be due to the fact that during cooling the particles start precipitating. This results in a change of the effective cluster size and the volume fraction which can lead to a change in the effective inter-particle interaction.

SAXS data fit for BSA-YCl_3 samples: Typical fits for the BSA-YCl_3 samples with c_p = 100 mg/ml and c_s = 10 mM and 100mM are represented in Fig. S3 (a-b). The reduced second virial coefficients for these samples are shown in Fig. S3(c). In this case, one axis of the ellipsoidal particle is kept fixed at 18 Å and the other axis is not constrained [5].

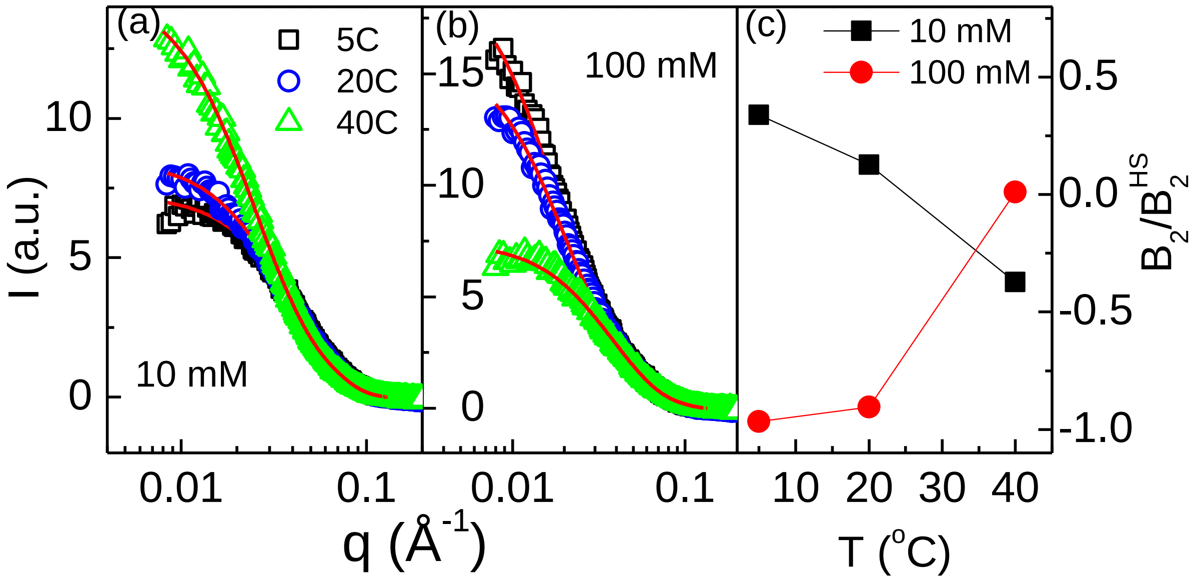

Figure S3: Typical fits (red solid lines) to the SAXS data (symbols) of the BSA-YCl_3 sample with c_p = 100 mg/ml, (a) c_s = 10 mM and (b) c_s = 100 mM at different temperatures as indicated by the legends, and (c) reduced second virial coefficient as a function of temperature for c_s = 10 mM (black symbols) indicating an increase in attraction with increasing temperature (similar to an LCST) and for c_s = 100mM (red symbols) indicating an increase in attraction with decreasing temperature (similar to a UCST). Error bars are smaller than the symbols.

We can see in Fig. S3(c) that the sample with low c_s (10mM) shows an increasingly attractive interaction with increasing temperature indicating the possibility of an LCST type behavior. On the other hand, the sample with high c_s (100 mM) exhibits an increase in attraction with decreasing temperature which indicates the possibility of a UCST behavior.

References:

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