

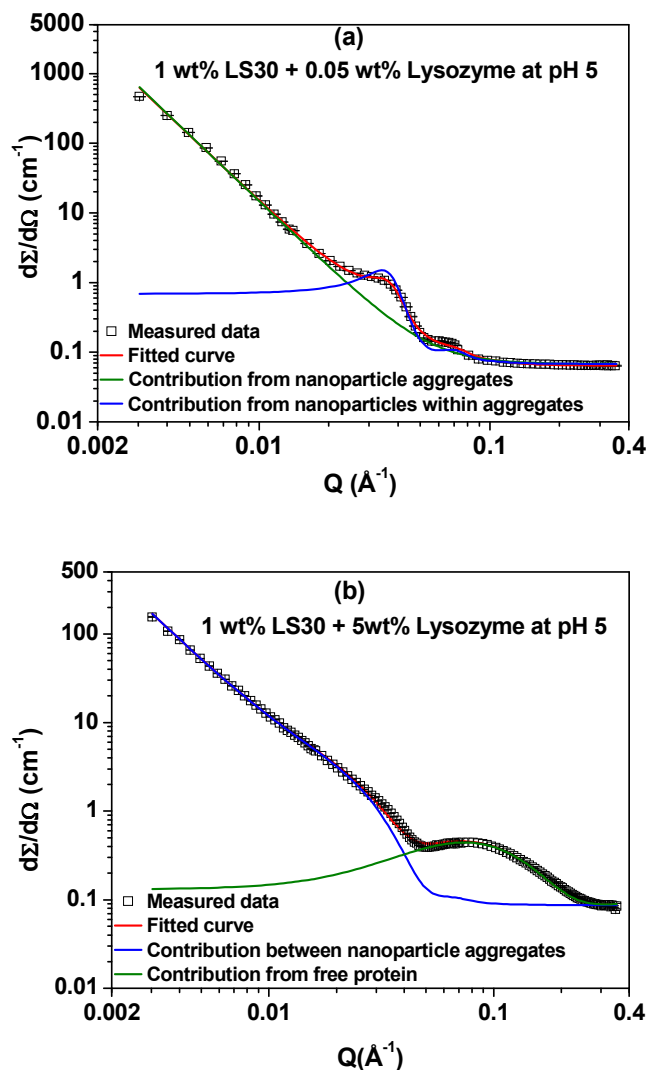
## Supporting Information

### pH Dependent Interaction and Resultant Structures of Silica Nanoparticles and Lysozyme Protein

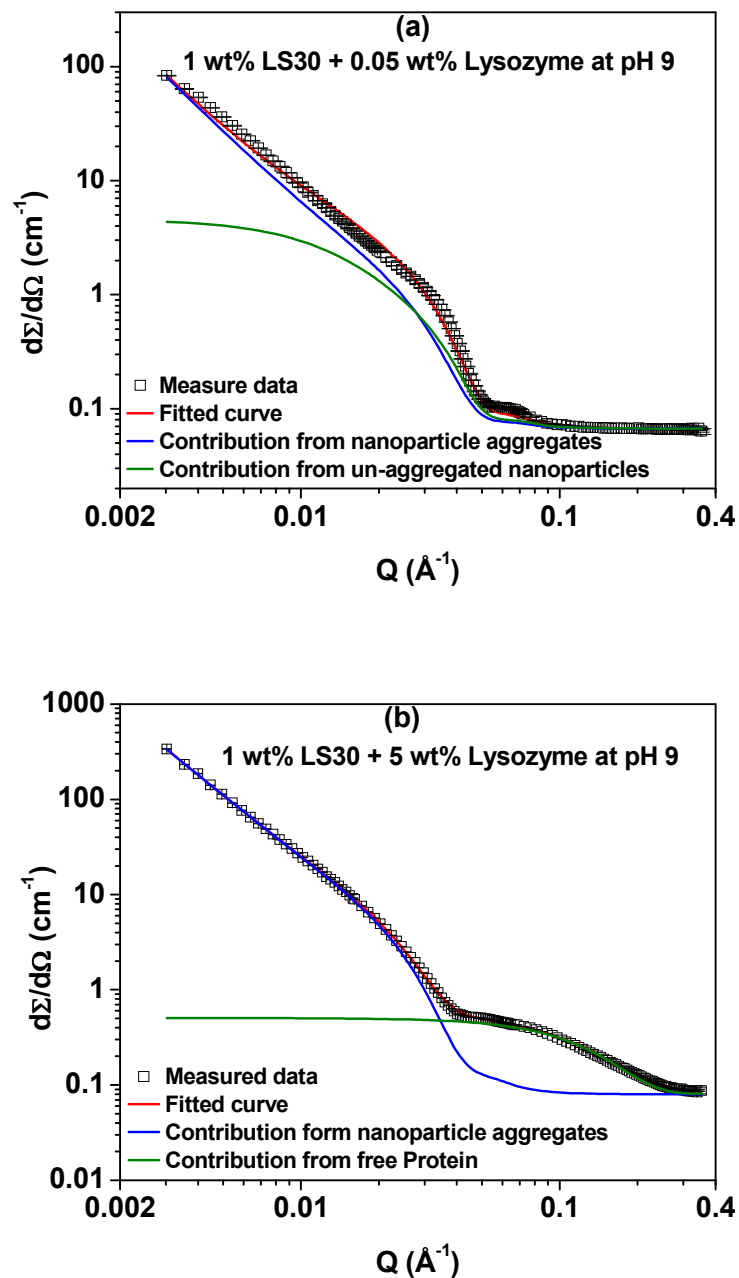
Sugam Kumar<sup>†</sup>, Vinod K. Aswal<sup>†,\*</sup> and P. Callow<sup>‡</sup>

<sup>†</sup>Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

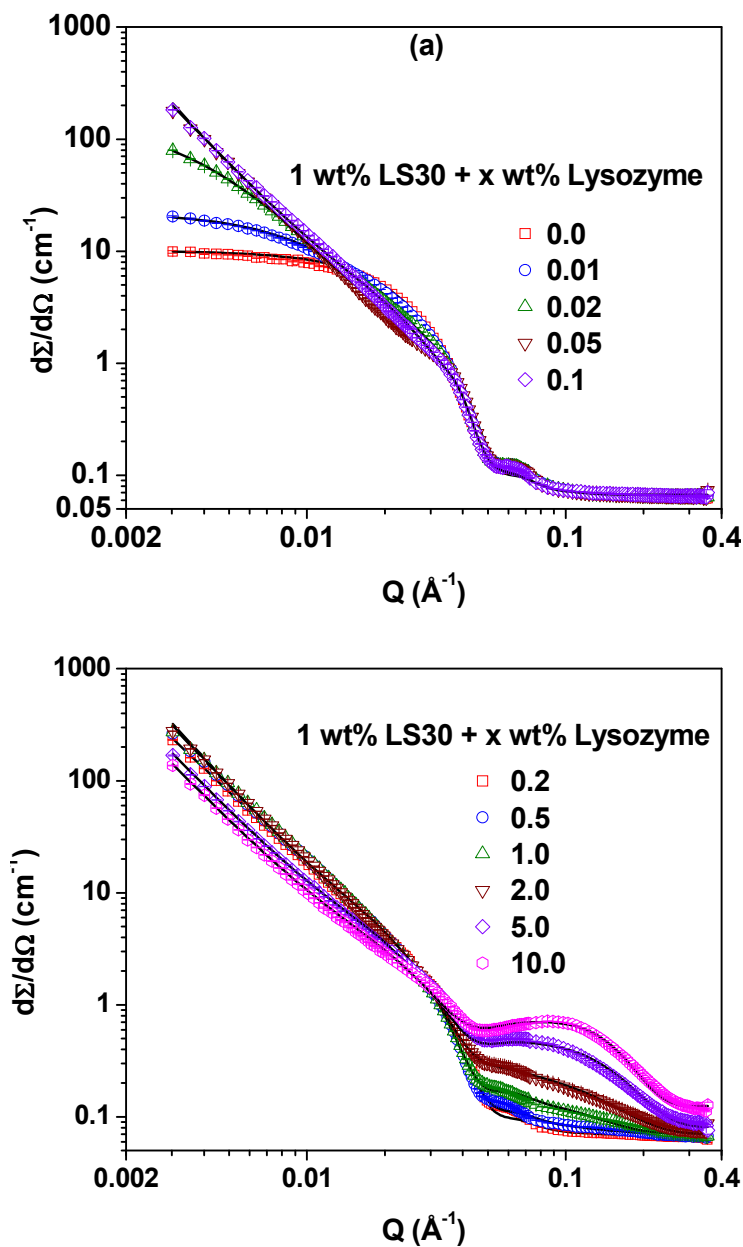
<sup>‡</sup>Institut Laue Langevin, 6 rue Jules Horowitz, B.P. 156, 38042 Grenoble Cedex 9, France



**Figure S1.** The calculated different contributions in the data fitting for (a) 1 wt% nanoparticles with 0.05 wt% protein at pH 5 where the nanoparticle aggregates are characterized by surface fractals (b) 1 wt% nanoparticles with 5wt% protein at pH 5 where the nanoparticle aggregates are characterized by mass fractals coexisting with free protein.



**Figure S2.** The calculated different contributions in the data fitting for (a) 1 wt% nanoparticles with 0.05 wt% protein at pH 9 where the nanoparticle aggregates are characterized by mass fractals coexisting with un-aggregated nanoparticles (b) 1 wt% nanoparticles with 5wt% protein at pH 9 where the nanoparticle aggregates are characterized by mass fractals coexisting with free protein.



**Figure S3.** SANS data of 1 wt% LS30 silica nanoparticle system with (a) lower protein concentration (0.0 to 0.1 wt%) and (b) higher protein concentration (0.2 to 10 wt%) at pH 7. The data are fitted by combining the scattering contributions from nanoparticle aggregates with un-aggregated nanoparticles for data set (a) and nanoparticle aggregates with free protein for data set (b).

**Table S1.** Fitted parameters of interaction of 1 wt% LS30 silica nanoparticle system with varying lysozyme protein concentration at pH 7.

(a) Low protein concentration regime

Concentration $C$ (wt%)	Particle radius $R_m$ (nm)	Building block radius $R_b$ (nm)	Fractal dimension $D$	Fraction of aggregated nanoparticles $\phi_{anp}$ (%)
0.0	$8.0 \pm 0.2$	-	-	0
0.01	$8.0 \pm 0.2$	$9.0 \pm 0.2$	$2.5 \pm 0.1$	24
0.02	$8.0 \pm 0.2$	$9.0 \pm 0.2$	$2.5 \pm 0.1$	43
0.05	$8.0 \pm 0.2$	$9.1 \pm 0.2$	$2.4 \pm 0.1$	80
0.1	$8.0 \pm 0.2$	$9.2 \pm 0.2$	$2.5 \pm 0.1$	100

(b) High protein concentration regime

Concentration $C$ (wt%)	Particle radius $R_m$ (nm)	Building block radius $R_b$ (nm)	Fractal dimension $D$	Fraction of free protein $\phi_{fp}$ (%)
0.2	$8.0 \pm 0.2$	$9.3 \pm 0.2$	$2.5 \pm 0.1$	24
0.5	$8.0 \pm 0.2$	$9.2 \pm 0.2$	$2.5 \pm 0.1$	48
1.0	$8.0 \pm 0.2$	$9.3 \pm 0.2$	$2.4 \pm 0.1$	60
2.0	$8.0 \pm 0.2$	$9.4 \pm 0.2$	$2.5 \pm 0.1$	69
5.0	$8.0 \pm 0.2$	$9.3 \pm 0.2$	$2.3 \pm 0.1$	75
10.0	$8.0 \pm 0.2$	$9.4 \pm 0.2$	$2.4 \pm 0.1$	82

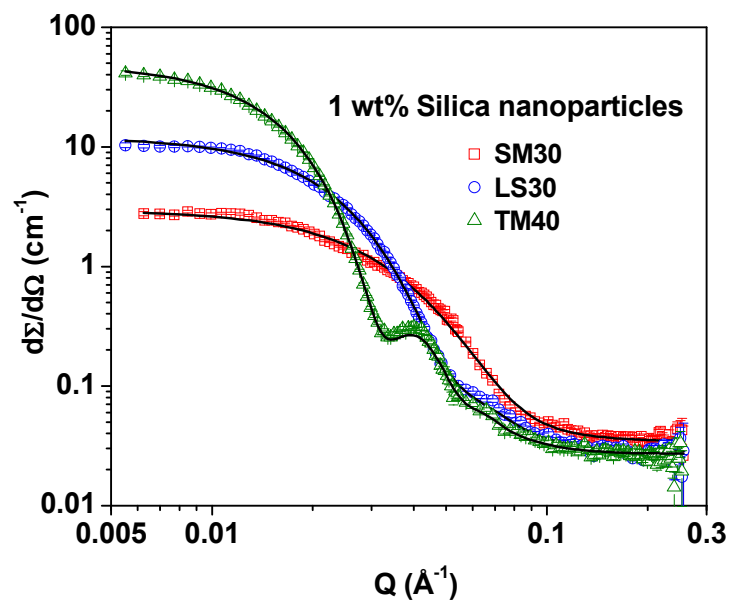
**Table S2.** The aggregate structure and free component present in 1 wt% LS30 silica nanoparticles with varying lysozyme protein concentrations (0.01, 0.1, 1.0 and 10.0 wt%) at three pH values (5, 7 and 9).

pH value	Protein concentration = 0.01 wt%		
	Aggregate structure		Free component
	Fractal morphology	Fractal dimension	
5	Surface	$2.7 \pm 0.1$	Nanoparticles
7	Mass	$2.5 \pm 0.1$	Nanoparticles
9	Mass	$2.1 \pm 0.1$	Nanoparticles

pH value	Protein concentration = 0.1 wt%		
	Aggregate structure		Free component
	Fractal morphology	Fractal dimension	
5	Surface	$2.8 \pm 0.1$	Protein
7	Mass	$2.5 \pm 0.1$	-
9	Mass	$2.1 \pm 0.1$	Nanoparticles

pH value	Protein concentration = 1.0 wt%		
	Aggregate structure		Free component
	Fractal morphology	Fractal dimension	
5	Surface	$2.7 \pm 0.1$	Protein
7	Mass	$2.4 \pm 0.1$	Protein
9	Mass	$2.1 \pm 0.1$	Protein

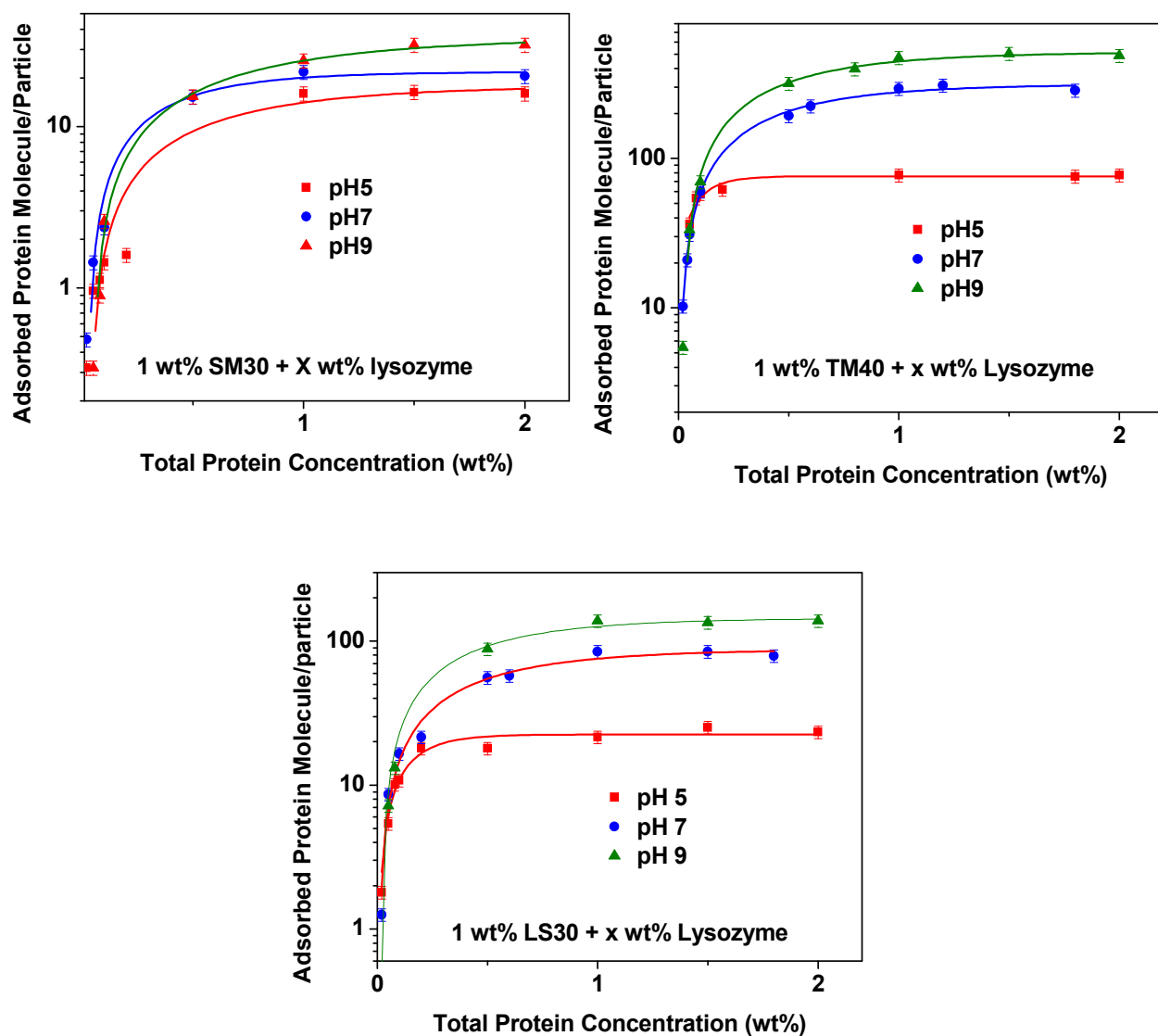
pH value	Protein concentration = 10.0 wt%		
	Aggregate structure		Free component
	Fractal morphology	Fractal dimension	
5	Mass	$2.5 \pm 0.1$	Protein
7	Mass	$2.4 \pm 0.1$	Protein
9	Mass	$2.1 \pm 0.1$	Protein



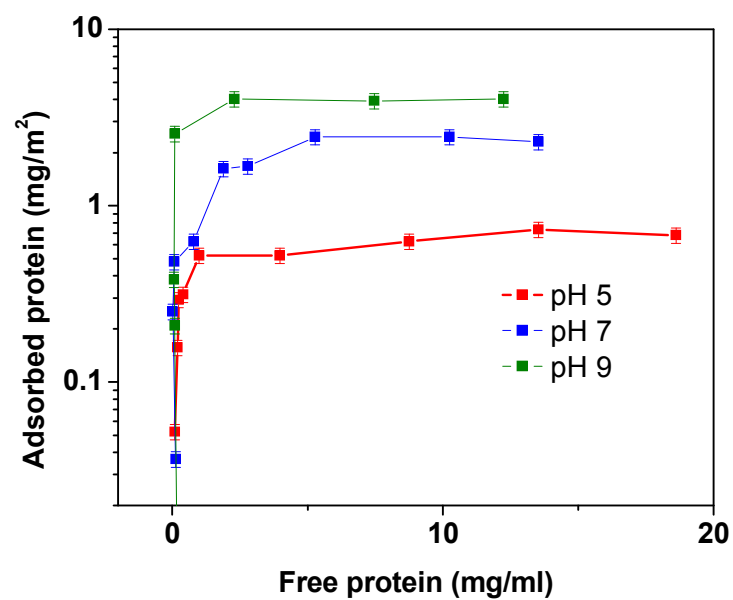
**Figure S4.** SANS data of 1 wt% different sized silica nanoparticle (SM30, LS30 and TM40) systems. All nanoparticle systems are fitted with a form factor of polydispersed spheres.

**Table S3.** Structural parameters of different silica nanoparticle systems.

Nanoparticle system	Mean radius $R_m(\text{nm})$	Polydispersity $\sigma$
SM30	$4.2 \pm 0.1$	$0.30 \pm 0.05$
LS30	$8.0 \pm 0.2$	$0.20 \pm 0.04$
TM40	$13.0 \pm 0.5$	$0.15 \pm 0.03$



**Figure S5.** Lysozyme protein adsorption curve on 1wt% (a) SM30 (8.4 nm) (b) TM40 (26.0) silica nanoparticles. These curves are expressed as number of adsorbed protein molecules per nanoparticle vs. total protein concentration at three pH values (5, 7 and 9). Solid lines are fits to the curves using an exponential equation.



**Figure S6:** Adsorption curve of lysozyme protein on 1wt% silica nanoparticles expressed in terms of adsorbed protein amount ( $\text{mg/m}^2$ ) vs. free protein ( $\text{mg/ml}$ ).



**Table S4.** Fitted structural parameters of complexes of 1 wt% lysozyme protein with 1 wt% different sized silica nanoparticles (SM30, LS30 and TM40) at three pH values (5, 7 and 9).

Nanoparticle System	Particle radius $R_m$ (nm)	Fractal morphology	Building block radius $R_b$ (nm)	Fractal dimension $D_s/D_m$	Adsorbed protein molecules/particle	Fraction of free protein $\phi_p$
pH 5						
SM30	$4.2 \pm 0.1$	Mass	$5.8 \pm 0.2$	$2.3 \pm 0.1$	15	52
LS30	$8.1 \pm 0.2$	Surface	$9.0 \pm 0.2$	$2.7 \pm 0.1$	36	80
TM40	$13.0 \pm 4.2$	Surface	$15.3 \pm 0.5$	$2.7 \pm 0.1$	77	90
pH 7						
SM30	$4.2 \pm 0.2$	Mass	$5.7 \pm 0.2$	$2.3 \pm 0.1$	20	35
LS30	$8.0 \pm 0.2$	Mass	$9.2 \pm 0.2$	$2.4 \pm 0.1$	76	58
TM40	$13.0 \pm 0.5$	Mass	$150.3 \pm 4.0$	$2.4 \pm 0.1$	294	62
pH 9						
SM30	$4.2 \pm 0.1$	Mass	$5.9 \pm 0.2$	$2.2 \pm 0.1$	26	20
LS30	$8.1 \pm 0.2$	Mass	$9.2 \pm 0.2$	$2.1 \pm 0.1$	151	28
TM40	$13.0 \pm 0.5$	Mass	$15.0 \pm 0.5$	$2.3 \pm 0.1$	464	40