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Dynamic Phase Diagram of Soft Nanocolloids Supplemental Material

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SANS modeling

The small angle neutron scattering (SANS) scattering cross section $\frac{d\Sigma}{d\Omega}(Q)$ in absolute units [cm^{-1}] following core-shell model[1–3] in dilute solution is given by (cf. Eq. (3) of the main paper)

$$\begin{aligned}\left(\frac{d\Sigma}{d\Omega}\right)(Q) &= N_z\, I_{cs}(Q)\\ &= N_z\left[I_{\rm core}(Q)+I^b_{\rm corona}(Q)+I_{\rm inter}(Q)+I_{\rm blob}(Q)\right]\\ &= \frac{\phi}{V_m}\Bigg[V^2_{core}N^2_{agg}\Delta\rho^2_{core}A^2_{core}\\ &\quad +V^2_{corona}N_{agg}\left(N_{agg}-\frac{1}{1+\hat{\nu}}\right)\Delta\rho^2_{corona}A^2_{corona}\\ &\quad +2V_{core}V_{corona}N^2_{agg}\Delta\rho_{core}\Delta\rho_{corona}A_{core}A_{corona}\\ &\quad +V^2_{corona}N_{agg}\Delta\rho^2_{corona}\left(\frac{P_p(Q)}{1+\hat{\nu}P_p(Q)}\right)\Bigg] \qquad (1)\end{aligned}$$

where $\Delta\rho_{core}=\rho_{core}-\rho_{solvent}$ and $\Delta\rho_{corona}=\rho_{corona}-\rho_{solvent}$ are the contrast difference of the core and corona of the micelles with respect to the solvent and ρ_i the corresponding scattering length densities. V_{core} and V_{corona} are the volume per molecule of the insoluble core and soluble corona blocks, respectively defined as $V_i = M_i/(d_i N_A)$, with N_A the Avogadro's number, d_i the bulk density and M_i the molecular weight in g/mol of the core or corona blocks. $V_m = N_{agg}(V_{core}+V_{corona})$ as the micellar volume. $\hat{\nu}$ is an effective virial type excluded volume parameter that scales with the effective concentration of the corona chains. Following Svaneborg and Pedersen,[2,4] the blob scattering from swollen corona chains was modeled as $I_{\rm blob}(Q)$. In this model[2] the chains are considered to be self-avoiding and interact mutually by blobs and also with the homogeneous core following a hard sphere potential. The scattering amplitude from the core is given by

$$\begin{aligned}A_{core}(Q) &= \frac{\int_0^{R_c} dr4\pi r^2\frac{\sin(Qr)}{Qr}\varphi_{core}(r)}{\int_0^{R_c} dr4\pi r^2\varphi_{core}(r)}\exp\left(-\frac{c_s^2Q^2}{2}\right) \qquad (2)\\ &= 3\frac{sin(QR_c)-(QR_c)cos(QR_c)}{(QR_c)^3}\exp\left(-\frac{c_s^2Q^2}{2}\right)\end{aligned}$$

for a core density profile φ_{core}=1 (compact core). For strong segregation the core smearing parameter is generally kept c_s=0, causing no effective change in the scattering pattern.

The scattering amplitude from the corona or shell is given by

$$A_{corona}(Q) = \frac{\int_{R_c}^{R_m} dr4\pi r^2\frac{\sin(Qr)}{Qr}\varphi_{star}(r)}{\int_{R_c}^{R_m} dr4\pi r^2\varphi_{star}(r)}\exp\left(-\frac{s_s^2Q^2}{2}\right) \qquad (3)$$

Where $\varphi_{\rm star}(r)$ the star-like density profile. For a finite size of the corona, the limit is chosen to be the micellar radius R_m, instead of ∞, with s_s the smearing parameter for the corona. For the linear chain form factor one can use the Beaucage form factor[5,6] given

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by:

$$P_p(Q) = \exp\left(-\frac{Q^2R_g^2}{3}\right) + \frac{d_f}{R_g^{d_f}}\Gamma\left(\frac{d_f}{2}\right)\left[\frac{erf\left(R_gQk\sqrt{6}\right)^3}{Q}\right]^{d_f} \quad (4)$$

Where, $k = 1.06$, Γ is the Gamma function and d_f is the fractal dimension of the scattering particle, $1 \leq d_f \leq 3$. In this approach a polymer chain is considered as a mass fractal characterized by a single spatial length scale, the radius of gyration R_g of the linear chain, and a fractal dimension for polymers in good solvent is typically $d_f = 1.7$. The first term in Eq.(4) is from the Guinier expression[7].

DLS and rheology modeling

For dynamic light scattering (DLS) our data analysis of the experimental intensity auto correlation function (IACF) $g_e^{(2)}(Q,t)$ was based on the inverse-Laplace transformation by *CONTIN* algorithm developed by Provencher[8,9] i.e.

$$g_e^{(1)}(Q,t) = \frac{1}{2\pi}\int_0^\infty d\Gamma G(\Gamma)\exp(-\Gamma t) \quad (5)$$

where $\Gamma = DQ^2$, with D the diffusion coeffecient of the scattering particles. We use the *CONTIN* algorithm as provided by the ALV-software.

To yield the zero-shear viscosity η_0 and to investigate the shear rate dependent viscosity (*shear thinning*) the Carreau equation[10] is used, which is given by:

$$\frac{\eta(\dot{\gamma}) - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{[1 + (\dot{\gamma}/\dot{\gamma}_c)^a]^{\frac{1-b}{a}}} \quad (6)$$

Where η_∞ denotes high shear rate Newtonian limit of viscosity. Frequently the high shear rate region is not observed, and η_∞ is set to zero in Eq.(6). $\dot{\gamma}_c$ indicates the onset of the shear thinning and has the dimensions of s^{-1}; the power law exponent, $(1-b)$, describes the dependence of the viscosity on shear rate in the shear thinning region. For our samples the value of $(1-b)$ lies between 0.2 to 0.76 at intermediate concentration for $\phi < \phi_m^*$. It is to be noted that, for dilute concentration $(1-b) = 0$, gives the Newtonian plateau with zero-shear viscosity η_0. The additional dimensionless parameter 'a' represents the width of the transition region between the constant Newtonian plateau observed at low shear rates and the asymptotic power law decrease of the viscosity found at high shear rates. Value of $a = 2$ is kept constant.

The Krieger-Dougherty (KD) model for solutions of spherical suspensions, it is given by :

$$\frac{\eta_0(\phi)}{\eta_{solv}} = \left(1 - \frac{\phi_{eff}}{\phi_{lim}}\right)^{-\varepsilon} \quad (KD) \quad (7)$$

Here $\phi_{eff} = \phi$, the effective volume fraction and $\varepsilon = [\eta] \times \phi_{lim}$, and Martin relations for solutions of spherical suspensions

$$\frac{\eta_0(\phi)}{\eta_{solv}} = 1 + [\eta]\phi e^{[\eta]K\phi} \quad (Martin\ relation) \quad (8)$$

for $\phi > \phi^*$. Here, K is a constant and $[\eta] = (\eta_0 - \eta_{solv})/(\eta_{solv}\phi)$ is the intrinsic viscosity in the limit $\phi \to 0$, of the system[11].

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