

Supporting Information for:

Effect of salt on formation and stability of water-in-oil Pickering nanoemulsions stabilized by diblock copolymer nanoparticles

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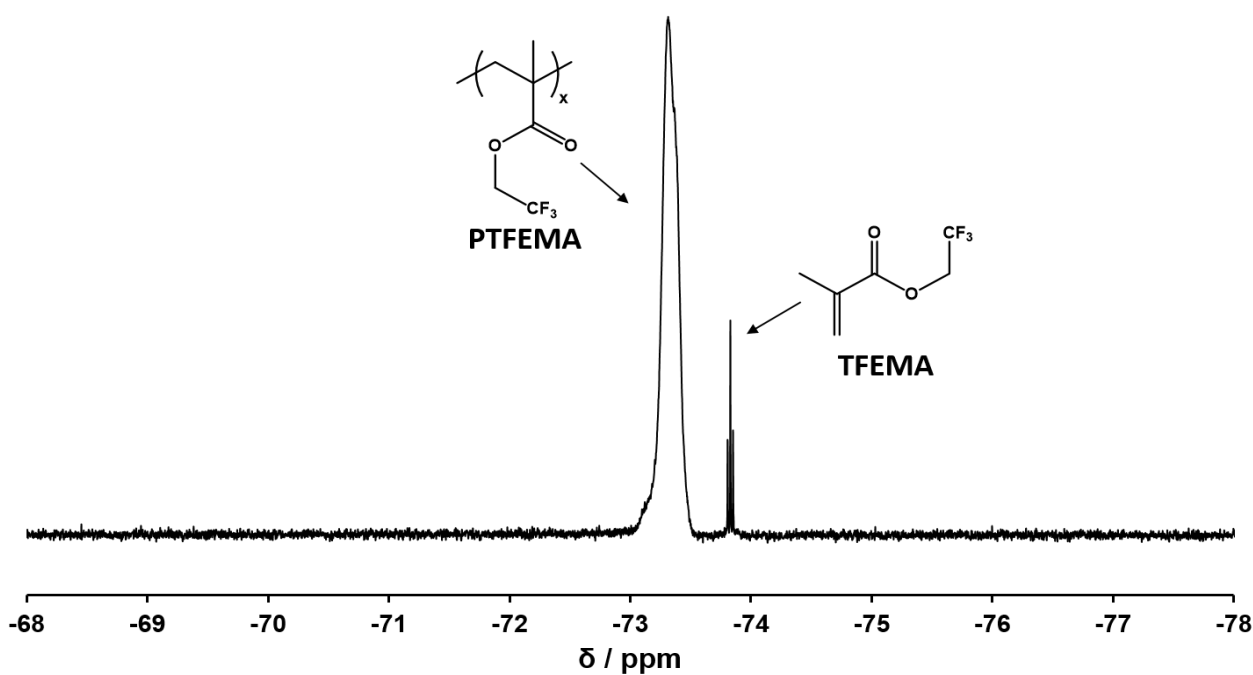


Figure S1. ^{19}F NMR spectrum recorded for PSMA₃₂-PTFEMA₅₃ diblock copolymer dissolved in CDCl_3 . From the residual monomer signal observed at -73.8 ppm, a final TFEMA conversion of 97% can be calculated.

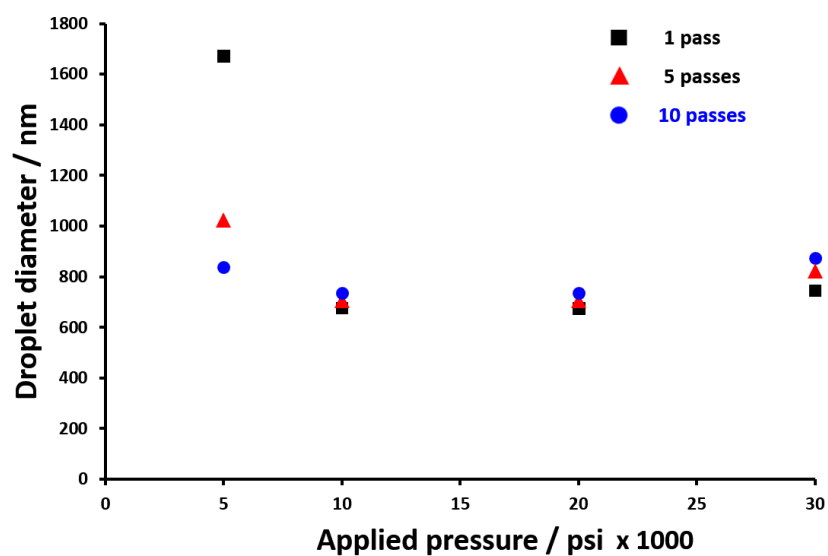


Figure S2. Effect of varying the applied pressure and number of passes during microfluidization on the initial z-average aqueous droplet diameter of w/o Pickering nanoemulsions prepared using 5.0% w/w PSMA₃₂-PTFEMA₅₃ nanoparticles at a fixed water volume fraction of 0.10, as determined by DLS.

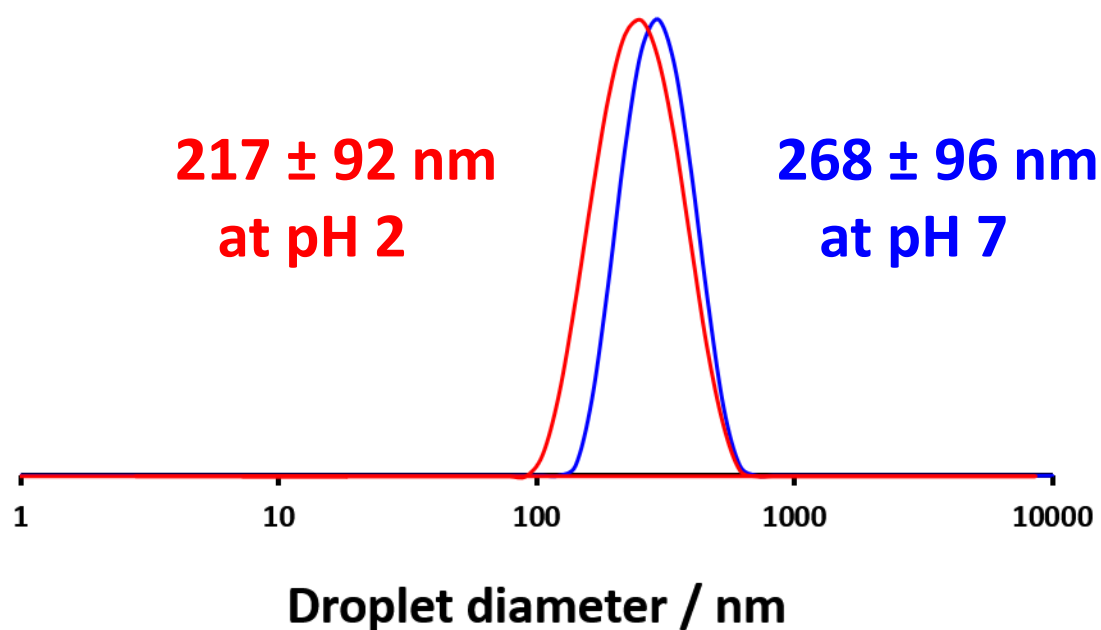


Figure S3. Intensity-average droplet size distributions recorded by DLS for Pickering nanoemulsions prepared using either a neutral (pH 7) or acidic (pH 2) aqueous solution containing 0.11 M NaCl.

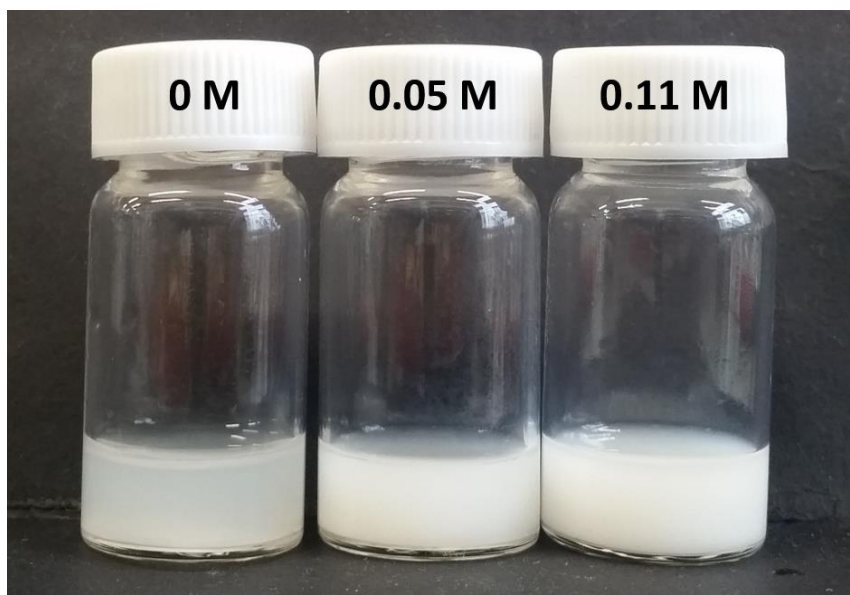


Figure S4. Digital photographs recorded for one-day-old w/o Pickering nanoemulsions prepared using various NaCl concentrations (0, 0.05 or 0.11 M) at a constant nanoparticle concentration of 5.0% w/w and a water volume fraction of 0.10. Microfluidization conditions: applied pressure = 10 000 psi; 5 passes.

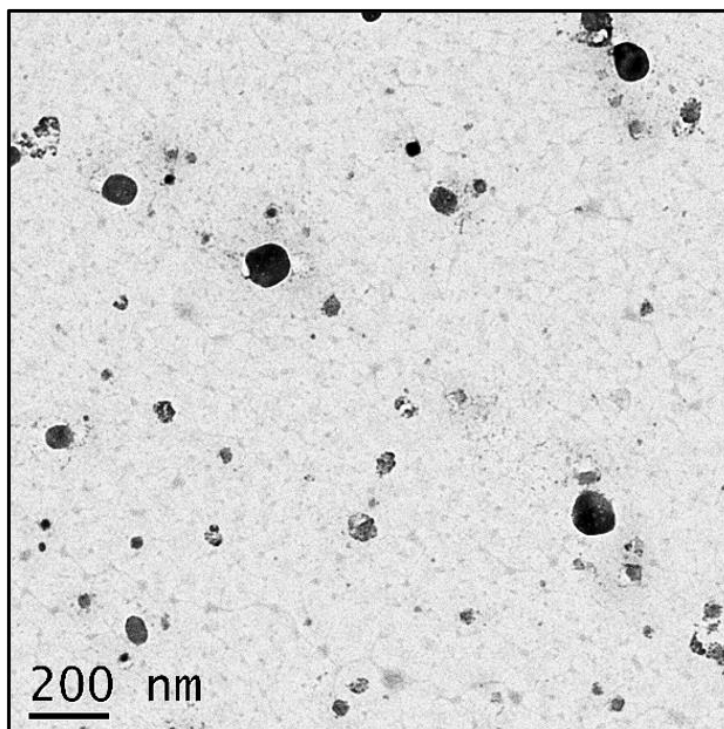


Figure S5. Representative TEM image recorded for dried water-in-*n*-dodecane Pickering nanoemulsions prepared using 5.0% w/w PSMA₃₂-PTFEMA₅₃ nanoparticles with 0.11 M NaCl dissolved in the aqueous phase. Conditions: microfluidization pressure = 10 000 psi; 5 passes.

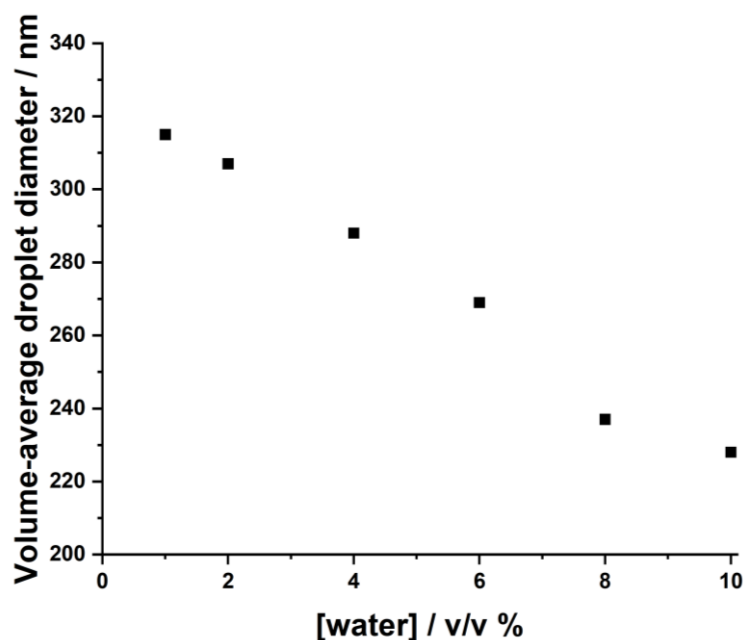


Figure S6. Effect of varying the aqueous droplet concentration on the apparent droplet diameter of a water-in-*n*-dodecane Pickering nanoemulsion as determined by analytical centrifugation (LUMiSizer instrument). This so-called ‘hindrance’ function indicates that the optimum droplet concentration for such analyses is approximately 1.0% v/v, with higher concentrations leading to hindered creaming and hence undersizing.

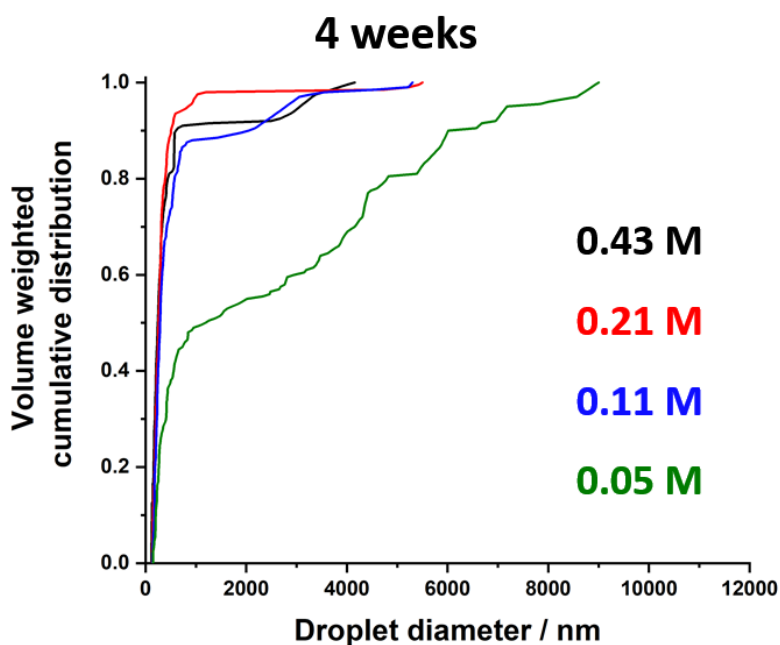


Figure S7. Volume-weighted cumulative distributions determined by analytical centrifugation (LUMiSizer instrument) for *n*-dodecane-in-water Pickering nanoemulsions prepared using various amounts of NaCl dissolved in the aqueous phase) after ageing for 4 weeks at 20 °C.

Structural models for SAXS analysis

In general, the X-ray intensity scattered by a system composed of n different (non-interacting) populations of polydisperse objects [usually described by the differential scattering cross-section per unit sample volume, $d\Sigma(q)/d\Omega$] can be expressed as:¹

$$\frac{d\Sigma(q)}{d\Omega} = \sum_{l=1}^n S_l(q) N_l \int_0^\infty \dots \int_0^\infty F_l(q, r_{l1}, \dots, r_{lk})^2 \Psi_l(r_{l1}, \dots, r_{lk}) dr_{l1} \dots dr_{lk} \quad S1$$

where $F_l(q, r_{l1}, \dots, r_{lk})$ is the form factor, $\Psi_l(r_{l1}, \dots, r_{lk})$ is the distribution function, N_l is the number density per unit volume and $S_l(q)$ is the structure factor of the l^{th} population in the system. Here, r_{l1}, \dots, r_{lk} is a set of k parameters describing the structural morphology of the l^{th} population.

Spherical Micelle SAXS Model

In terms of Equation S1, a dispersion of spherical micelles formed by an amphiphilic diblock copolymer can be described as a single population system ($n = 1$). Assuming that only the micelle core radius is polydisperse, Equation S1 for this system can be rewritten as:

$$\frac{d\Sigma(q)}{d\Omega} = S_1(q) N_1 \int_0^\infty F_1(q, r_{11})^2 \Psi_1(r_{11}) dr_{11} \quad S2$$

The spherical micelle form factor for Equation S2 is given by:¹

$$F_1(q, r_{11}) = N_s^2 \beta_s^2 A_s^2(q, r_{11}) + N_s \beta_c^2 F_c(q, R_g) + N_s (N_s - 1) \beta_c^2 A_c^2(q) + 2 N_s^2 \beta_s \beta_c A_s(q, r_{11}) A_c(q) \quad S3$$

where r_{11} is the spherical micelle core radius, R_g is the radius of gyration of the PSMA coronal block, and the X-ray scattering length contrast for the core and corona blocks is given by $\beta_s = V_s(\xi_s - \xi_{\text{sol}})$ and $\beta_c = V_c(\xi_c - \xi_{\text{sol}})$, respectively. Here ξ_s , ξ_c and ξ_{sol} are the X-ray scattering length densities of the core block ($\xi_{\text{PTFEMA}} = 12.76 \times 10^{10} \text{ cm}^{-2}$), the corona block ($\xi_{\text{PSMA}} = 9.24 \times 10^{10} \text{ cm}^{-2}$) and the solvent ($\xi_{\text{sol}} = 7.63 \times 10^{10} \text{ cm}^{-2}$), respectively. V_s and V_c are volumes of the core block (V_{PTFEMA}) and the corona block (V_{PSMA}), respectively. The volumes were calculated from $V = \frac{M_{n,\text{pol}}}{N_A \rho}$ using the solid-state homopolymer densities of PTFEMA ($\rho_{\text{PTFEMA}} = 1.47 \text{ g cm}^{-3}$)² and PSMA ($\rho_{\text{PSMA}} = 0.97 \text{ g cm}^{-3}$)³ determined by helium pycnometry, where $M_{n,\text{pol}}$ corresponds to the number-average molecular weight of the block. The aggregation number of spherical micelles is expressed as $N_s = \frac{\frac{4}{3}\pi r_{11}^3}{V_s}$ where it is assumed that the solvent is absent in the micelle core. The sphere form factor amplitude is used for the amplitude of the core self-term:

$$A_c(q, r_{11}) = \Phi(qr_{11}) \exp\left(-\frac{q^2 \sigma^2}{2}\right) \quad S4$$

where

$$\Phi(x) = \frac{3[\sin(x) - x \cos(x)]}{x^3} \quad S5$$

A sigmoidal interface between the two blocks was assumed for the spherical micelle form factor (Equation S4). This is described by the exponent term with a width σ accounting for a decaying scattering length density at the membrane surface. This σ value was fixed at 0.25 nm during fitting.

The form factor amplitude of the spherical micelle corona in Equation S3 is given by:

$$A_c(q) = \frac{\int_{R_s}^{R_s+2s} \mu_c(r) \frac{\sin(qr)}{qr} r^2 dr}{\int_{R_s}^{R_s+2s} \mu_c(r) r^2 dr} \exp\left(-\frac{q^2 \sigma^2}{2}\right) \quad S6$$

The radial profile, $\mu_c(r)$, can be expressed by a linear combination of two cubic b splines, with two fitting parameters s and a corresponding to the width of the profile and the weight coefficient, respectively. This information can be found elsewhere,⁴⁻⁵ as can the approximate integrated form of Equation S5. The self-correlation term for the corona block is given by the Debye function:

$$F_c(q, R_g) = \frac{2[\exp(-q^2 R_g^2) - 1 + q^2 R_g^2]}{q^4 R_g^4} \quad S7$$

The structure factor in Equation S2, $S_1(q)$, is usually expressed for interacting spherical micelles as:⁶

$$S_1(q) = 1 + \frac{A_1^{\text{av}}(q, r_{11})^2 [S_{\text{PY}}(q, R_{\text{PY}}, f_{\text{PY}}) - 1]}{F_1(q, r_{11})} \quad S8$$

Herein the form factor of the average radial scattering length density distribution of micelles is expressed as $A_1^{\text{av}}(q, r_1) = N_s [\beta_s A_s(q, r_{11}) + \beta_c A_c(q)]$ and $S_{\text{PY}}(q, R_{\text{PY}}, f_{\text{PY}})$ is a hard-sphere interaction structure factor solved using the Percus-Yevick closure relation,^{1,7} where R_{PY} is the interaction radius and f_{PY} is the hard-sphere volume fraction. For dilute dispersions of micelles it is assumed that $S_{\text{PY}}(q, R_{\text{PY}}, f_{\text{PY}}) = 1$.

A polydispersity of the micelle radius in Equation S2 can be described by a Gaussian distribution:

$$\Psi_1(r_{11}) = \frac{1}{\sqrt{2\pi\sigma_{R_s}^2}} \exp\left(-\frac{(r_{11} - R_s)^2}{2\sigma_{R_s}^2}\right) \quad S9$$

where R_s is the mean of the micelle core radius and σ_{R_s} is its standard deviation. The number density per unit volume for the micelle model is expressed as:

$$N_1 = \frac{\varphi_1}{\int_0^\infty V(r_{11})\Psi(r_{11})dr_{11}} \quad S10$$

where φ_1 is the total volume fraction of copolymer in the spherical micelles and $V(r_{11})$ is the total volume of copolymer in a spherical micelle [$V(r_{11}) = (V_s + V_c)N_s$].

Assuming that the projected contour length of a PSMA monomer is 0.255 nm (two C-C bonds in *all-trans* conformation), the total contour length of a PSMA₃₂ block, $L_{\text{PSMA32}} = 32 \times 0.255 \text{ nm} = 8.16 \text{ nm}$. Given a mean Kuhn length of 1.53 nm (based on the known literature value for PMMA⁸) an estimated unperturbed radius of gyration, $R_g = (8.16 \times 1.53/6)^{0.5} = 1.44 \text{ nm}$ is calculated. The data fit to the SAXS pattern recorded for PSMA₃₂-PTFEMA₅₃ spheres using the spherical micelle suggested that the experimental R_g for the corona PSMA block (1.72 nm) is physically reasonable, since it is close to this theoretical estimate.

Two-population SAXS Model

In order to construct a structural model for the SAXS analysis of water-in-oil emulsion droplets stabilised by PSMA₃₂-PTFEMA₅₃ spherical micelles, a previously used formalism for core-particulate shell spherical particles was employed.⁹ It was assumed that the differential cross-section per unit sample volume for the studied system patterns can be represented as a sum of two terms corresponding to scattering signals generated by two populations ($n = 2$ in Equation S1): spherical micelles forming the particulate shell (the first population, $l = 1$ in Equation S1) and core-shell particles (the second population, $l = 2$ in Equation S1). The contribution to the scattering signal from the first population can be described by the same term used for the spherical micelle dispersion (Equation S2). By expressing the scattering signal from the second population in a similar manner to that of the first population, the differential scattering cross-section per unit sample volume of the whole system could be written as:

$$\frac{d\Sigma(q)}{d\Omega} = S_1(q)N_1 \int_0^\infty F_1(q, r_{11})^2 \Psi_1(r_{11}) dr_{11} + S_2(q)N_2 \int_0^\infty F_2(q, r_{21})^2 \Psi_2(r_{21}) dr_{21} \quad S11$$

where it is assumed that only the particle core radius is polydisperse. The form factor for the second population, corresponding to the core-shell particles, is given by:

$$F_2(q, r_{21}) = V_{\text{total}}(\xi_{\text{shell}} - \xi_{\text{sol}})\Phi[q(r_{21} + T_{\text{shell}})] + V_{\text{core}}(\xi_{\text{core}} - \xi_{\text{shell}})\Phi(qr_{21}) \quad S12$$

where r_{21} is the core radius and T_{shell} is the shell thickness. $V_{\text{total}} = \frac{4}{3}\pi(r_{21} + T_{\text{shell}})^3$ and $V_{\text{core}} = \frac{4}{3}\pi r_{21}^3$

are volumetric parameters for the core-shell particles, while ξ_{core} , ξ_{shell} and ξ_{sol} are the scattering length densities for the aqueous droplets [$\xi_{\text{H}_2\text{O}} = 9.42 \times 10^{10} \text{ cm}^{-2}$], the particulate worm shell [volume-averaged scattering length density of the spherical micelles $\bar{\xi}_{\text{mic}} = (\xi_{\text{PSMA}}V_s + \xi_{\text{PTFEMA}}V_c)/(V_s + V_c)$] and the solvent ($\xi_{\text{n-dodecane}} = 7.63 \times 10^{10} \text{ cm}^{-2}$), respectively. As for population 1, a Gaussian distribution is assumed for the particle core radius (with a mean radius R_c and its standard deviation σ_{Rc}):

$$\Psi_2(r_{21}) = \frac{1}{\sqrt{2\pi\sigma_{Rc}^2}} e^{-\frac{(r_{21}-R_c)^2}{2\sigma_{Rc}^2}} \quad S13$$

Thus, the number density, N_2 , of the second population in Equation S11 is expressed as

$$N_2 = \frac{\varphi_2}{\int_0^\infty V(r_{21})\Psi_2(r_{21})dr_{21}} \quad S14$$

where φ_2 is the volume fraction of core-shell particles (i.e., nanoparticle-stabilized aqueous droplets) within the w/o nanoemulsion. Since the φ_2 used for the SAXS measurements is relatively low (0.01) and the q range resolved in the SAXS experiment (Figure 7) is virtually unaffected by the inter-droplet interactions, it was assumed that the structure factor was equal to unity [$S_2(q) = 1$]. However, since the nanoparticles (a.k.a. spherical micelles) are expected to form reasonably close-packed layer at the surface of the aqueous droplets (Figure 6b), a structure factor for the first population [$S_1(q)$], as represented by Equation S8, had to be used in the analysis.

References

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