Supporting Information

Microstructure of ionic liquid (EAN)-rich and oil-rich microemulsions studied by SANS

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Scattering Theory

For a sample consisting of an ensemble of scattering particles, the scattering intensity I(q) can be modeled using the decoupling approximation [1] according to

$$I(q) = n \cdot P(q) \cdot S(q)\,. \qquad \text{(SI-1)}$$

Here n is the particle number density, $P(q)$ the form factor and $S(q)$ the structure factor. For polydisperse spherical droplets the number density is given by

$$n = \frac{\phi_{c,i} a_c}{4\pi v_c (R_0 + \sigma)^2}\,, \qquad \text{(SI-2)}$$

where v_c is the volume per $C_{12}E_3$ molecule set to v_C = 568 Å^3, a_c is the area per $C_{12}E_3$ molecule at the EAN/*n*-alkane interface set to 64 Å^2 [2] and $\phi_{c,i}$ corresponds to the volume fraction of $C_{12}E_3$ at the interface. Assuming a certain polydispersity σ, R_0 is the mean radius of a particle. For cylindrical droplets the particle number density is given by

$$n = \frac{\phi_{c,i} a_c}{2\pi v_c R_0 (L_0 + R_0)}, \tag{SI-3}$$

where R_0 and L_0 correspond to the average cross section radius and the length of the cylinder, respectively [3].

Taking into account a diffuse scattering length density distribution, the form factor of a monodisperse spherical core-shell particle can be written as

$$P_{\text{monodisp}}(q) = \left[4\pi \int_0^\infty \left(f_{droplet}(r) \Delta\rho_{\text{film}} \right) r^2 \frac{\sin(qr)}{qr} dr \right]^2, \tag{SI-4}$$

where $f_{\text{droplet}}(r)$ is the radial scattering length density distribution function [4]

$$f_{\text{droplet}}(r) = \frac{1}{\exp\left(\frac{r - R - d/2}{\chi} \right) + 1} - \frac{1 - \Delta\rho_{core} / \Delta\rho_{film}}{\exp\left(\frac{r - R + d/2}{\chi} \right) + 1} \tag{SI-5}$$

where $\Delta\rho_{\text{core}} = \rho_{\text{bulk}} - \rho_{\text{core}}$ and $\Delta\rho_{\text{film}} = \rho_{\text{bulk}} - \rho_{\text{film}}$ are the scattering length density differences (i.e. the adjusted contrast condition), R is the radius of a droplet, and d is a measure of the thickness of the amphiphilic film, which is in the range of the molecular length of a single surfactant molecule. The parameter χ is a measure for the sharpness of the scattering length density profile. For $\chi \approx 0$ the profile is sharp, while for larger values of χ, the scattering length density at the internal interface changes smoothly. The polydispersity is taking into account convoluting the form factor P_{monodisp} of monodisperse spherical core-shell particle with a *Gaussian* distribution of the radius R around its mean value R_0 according to

$$P_{\text{sphere}}(q) = \int_0^\infty P_{\text{monodisp}}(q, r, R)\, W_{\text{R}}(R, R_0, \sigma_{\text{R}})\, dr dR \tag{SI-6}$$

with

$$W_{\text{R}} = \frac{1}{\sqrt{2\pi}\sigma_{\text{R}}} \exp\left[- \frac{(R - R_0)^2}{2\sigma_{\text{R}}^{\;2}} \right], \tag{SI-7}$$

where $2\sigma_R$ indicates the width of the distribution, which together with the mean radius R_0 defines the polydispersity index $p = \sigma_R/R_0$. The form factor of cylindrical microemulsion droplets with a mean cross section radius R_0 and the length L_0 can be separated into an axial term P_{rod} and a cross section term P_{cross} according to

$$P_{cylinder}(q) = L_0^2 \int_0^\infty dL\, P_{rod}(q) W_L(L, L_0, \sigma_L) \int_0^\infty dR\, P_{cross}(q) W_R(R, R_0, \sigma_R) \tag{SI-8}$$

where σ_L and σ_R correspond to the polydispersity of length and cross sectional radius, respectively. Assuming a Gaussian distribution, W_R is given by equation SI-7 and W_L is

$$W_L = \frac{1}{\sqrt{2\pi}\sigma_L} \exp\left[-\frac{(L-L_0)^2}{2\sigma_L{}^2}\right]. \tag{SI-9}$$

Note, that in alternative model the distribution of the cylinder length is described by an exponentially decaying function [5]. The axial term $P_{rod}(q)$ is given by the form factor of an orientationally averaged, infinitely thin rod of length L_0 [3] according to

$$P_{rod}(q) = \frac{2Si(qL)}{qL} - \frac{4(\sin 0.5qL)^2}{(qL)^2} \tag{SI-10}$$

where $Si(qL)$ is the sine integral function of qL. The cross section term is given by

$$P_{cross}(q) = \left[2\pi \cdot \Delta\rho_{film} \int_0^\infty r \cdot f_{droplet}(r, R_0) J_0(qr)\, dr\right]^2 \tag{SI-11}$$

with the zeroth order *Bessel* function of the first kind $J_0(qr)$.

Determination of the radius of inhomogeneous spherical droplets from the PDDF curve:

In order to extract the droplet radius from a PDDF curve one has to be aware of the fact that not only the shape but also the internal structure determines the shape of the PDDF and the position of the maximum. Full spheres provide symmetric PDDFs, where the position of the maximum indicates the radius of the droplets. However, Glatter showed [6], that for inhomogeneous spheres, the shape of the PDDF becomes increasingly asymmetric if the ratio of droplet diameter D to film thickness δ is increased. Thereby the maximum of the PDDF is shifted to the right. Thus, for inhomogeneous spheres the position of the maximum does not correspond to the radius of the sphere. Glatter [6] calculated the PDDFs of spheres varying the ratio D/δ from 2 (full sphere) to 10 (hollow sphere). In Table SI 1 the ratio D/δ, $R_{\mathrm{PDDF,max}}$ (maximum of the PDDF) and ratio $R_{\mathrm{PDDF,max}}/R$ for spheres of radius R=200 extracted from [6] are compiled.

Table SI 1: Ratio D/δ, $R_{\mathrm{PDDF,max}}$ (maximum of the PDDF) and ratio $R_{\mathrm{PDDF,max}}/R$ for spheres of radius R=200 Å extracted from [1].

$\boldsymbol{D/\delta}$	$\boldsymbol{R_{\mathrm{PDDF,max}}}$**/Å**	**($\boldsymbol{R_{\mathrm{PDDF,max}}/R}$)**
2.0	200	1.0
2.5	240	1.2
5.0	275	1.4
10.0	325	1.6

In order to account for the inhomogeneity of the oil-in-EAN and EAN-in-oil droplets studied in this work we used the data of Glatter [6] to extract the radius R_{GIFT} from the PDDFs. In Figure SI 1 the ratio $R_{\mathrm{PDDF,max}}/R$ is plotted versus D/δ to determine the dependence of the position of the PDDF-maximum on the inhomogeneity of the spheres. The data can be described using a modified hyperbola according to

$$\frac{R_{\mathrm{PDDF,max}}}{R} = \frac{1.20\dfrac{D}{\delta}}{1+0.65\dfrac{D}{\delta}}\,. \tag{SI-12}$$

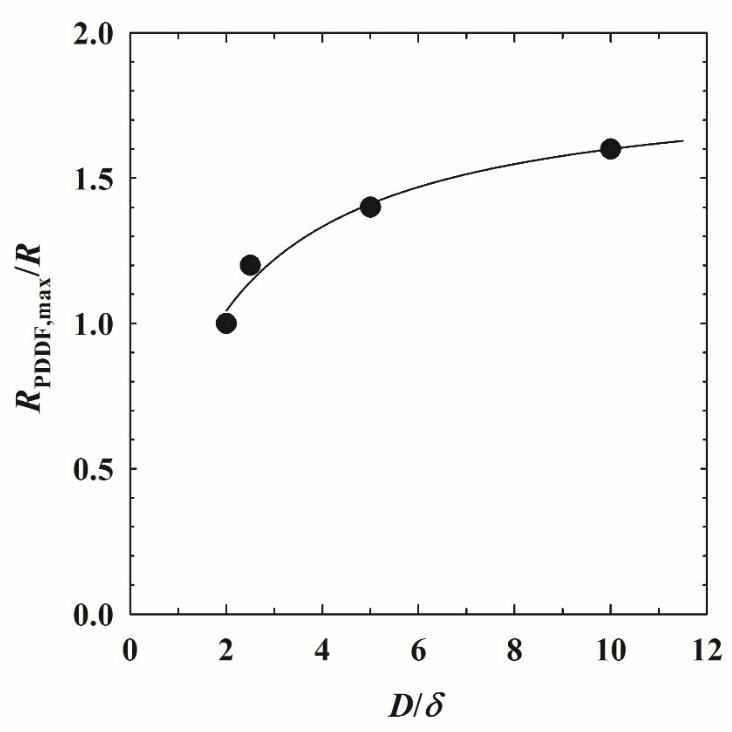

Figure SI 1: $R_{PDDF,max}/R$ plotted versus D/δ to determine the dependence of the position of the PDDF-maximum on the inhomogeneity of the spheres.

Using the position $R_{PDDF,max}$ of the PDDF maximum, the radius R_{FFA} and the film thickness ($d+\chi$) obtained from the form factor analysis, the radius R_{GIFT} arising from the GIFT analysis is given by

$$R_{GIFT} = \frac{R_{PDDF,max}\left(1 + 0.65\dfrac{2R_{FFA}}{d+\chi}\right)}{1.20\dfrac{2R_{FFA}}{d+\chi}}. \qquad \text{(SI-13)}$$

In Table SI 2 the parameters used in order to calculate the droplet radius R_{GIFT} from theposition $R_{\mathrm{PDDF,max}}$ of the PDDF maximum are compiled.

Table SI 2: Parameters used in order to calculate the droplet radii R_{GIFT} from the PDDF. The parameters are the radius R_{FFA} and the film thickness (d+χ) obtained from the form factor analysis as well as the location $R_{\mathrm{PDDF,max}}$ of the maximum of the PDDF.

EAN – *n*-dodecane – $C_{12}E_3$				**EAN – *n*-octane – $C_{12}E_3$**			
w_B	0.052	0.060	0.063	w_A	0.044	0.081	0.115
T / °C	31.2	34.1	36.5	T / °C	32.8	31.5	29.5
d / Å	4	4	4	d/ Å	8	9	8
χ / Å	2	2	2	χ / Å	6	6	6
R_{FFA} / Å	34	38	31	R_{FFA} / Å	52	47	54
$R_{\mathrm{PDDF,max}}$ / Å	46	62	50	$R_{\mathrm{PDDF,max}}$ / Å	52	64	80
R_{GIFT} / Å	28	38	31	R_{GIFT} / Å	34	43	52

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