Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting information for: Magnetic Microemulsions based on Magnetic Ionic Liquids

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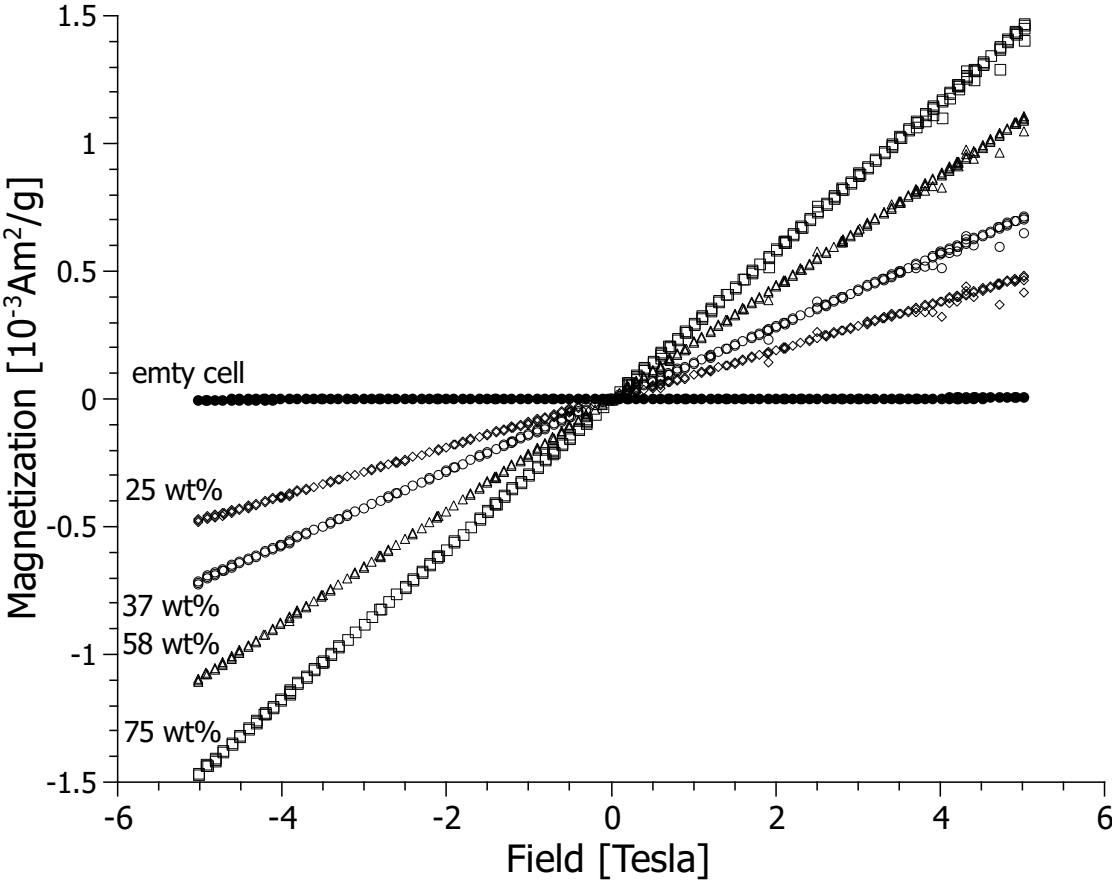

Figure S1: Example SQUID measurements of the microemulsions and the emty cell at 300 K. The labels indicate the wt% of MRTIL in the sample.

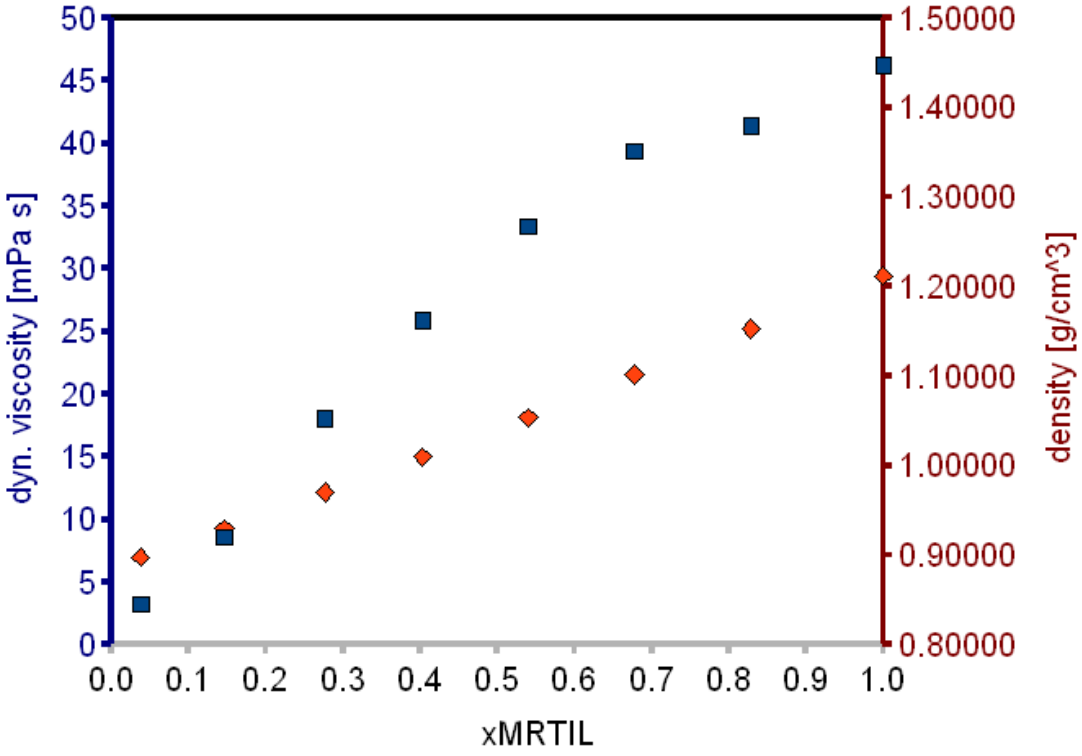

Figure S2: Dynamic viscosity (squares) and density (diamonds) of microemulsions with a constant amphiphile mass ratio (C_{16}mimCl+decanol) of 23 wt%.

Teubner-Strey Model

Fits were performed with the model introduced by Teubner and Strey[1] and expressed by Eq. 2.

As shown in Figure S3 and in the corresponding residuals in Figure S4, this model gives convincing fits mostly for the medium composition range of x_{MRTIL} of 0.3-0.65. For the other compositions systematic deviations are observed in the residuals. This is due to the fact that here apparently globular structures are present, that are not well described by the TS model. In addition, deviations at larger q arise from the fact that here the core-shell structure of the microemulsion droplets is seen, which is also not captured by the TS model. The small residuals at high x_{MRTIL} values are not an indication of a good agreement with the TS model but this results from the low overall coherent scattering intensity of these samples. This model cannot describe sufficiently the more complicated and soft surfactant layer which gives deviations between the model and the data points especially in the high q region.

Using Eq. 2d, $\langle \eta^2 \rangle$ was calculated for three different cases: MRTIL, surfactant and cosurfactant counts as one phase (case 1), all hydrocarbon chains of the surfactant/cosurfactant are belonging to the oil phase (case 3), partitioning of the hydrocarbon chains (case 2). Scattering length densities (SLD) were calculated as recommended by the National Institute of Standards and Technology (NIST) with

$$SLD = \frac{\sum_{i=1}^{n} b_{c_i}}{v_m} \tag{S1}$$

where b_{c_i} is the bound coherent scattering length of atom i (taken from[2]) in the chemical group with molecular volume v_m. Used densities and resulting SLD are summarized in Table S1. Resulting volume ratios and ρ for the two phases in case 1-3 were calculated under the assumption of invariant densities of chemical groups during mixing:

$$\Phi_{IL} = \sum \Phi_j \tag{S2}$$

$$\rho_{IL} = \frac{\sum(\Phi_j \cdot SLD_j)}{\Phi_{IL}} \tag{S3}$$

with the jth chemical group belonging to the IL phase. Φ_{oil} and ρ_{oil} where calculated analogously. The resulting $\langle \eta^2 \rangle$ are summarized in Table S2.

Table S1: Characteristic parameters of different chemical groups used to calculate values for $\langle \eta^2 \rangle$.

	parameters		location in IL/oil-phase		
chem. group	density/g cm^{-3}	SLD/10^{-4}nm^{-2}	case 1	case 2	case 3
bmim[$FeCl_4$]	1.36	1.55	1/0	1/0	1/0
D12-cyclohexane	0.89	6.68	0/1	0/1	0/1
-mimCl	1.45	2.41	1/0	1/0	1/0
decyl	0.79	-0.41	1/0	0.9/0.1	0/1
hexadecyl	0.82	-0.37	1/0	0.625/0.375	0/1
-OH	1.42	1.04	1/0	1/0	1/0

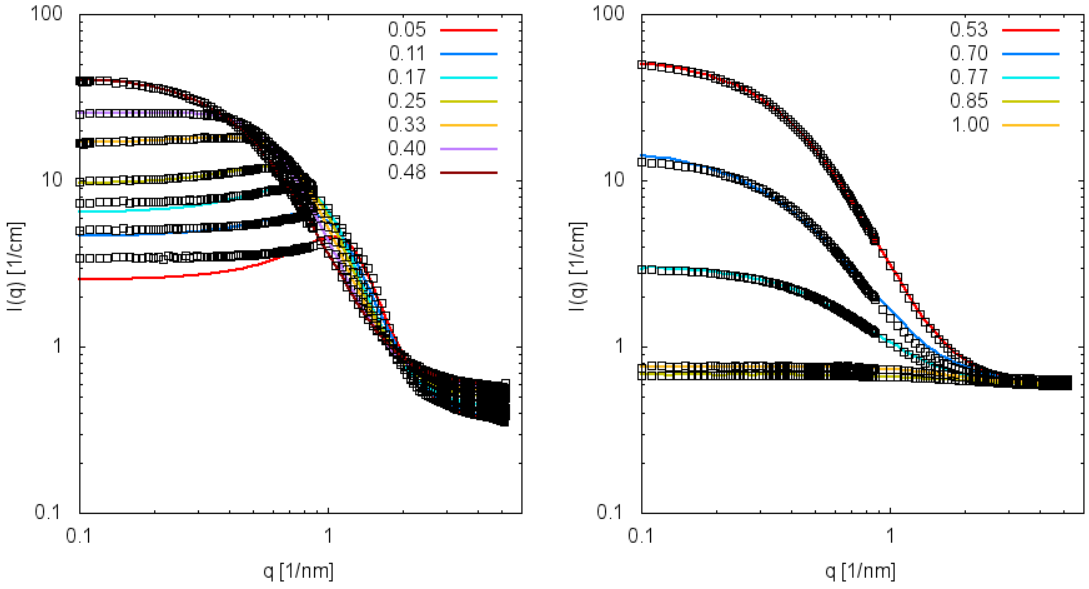

Figure S3: SANS curves with D12-cyclohexane as the oil phase. The samples are along the experimental path shown in Figure 1. Ratios between MRTIL and oil are x_{MRTIL}=0.05-0.48 (left) and x_{MRTIL}=0.53-1.00 (right). Lines are fits with the TS model.

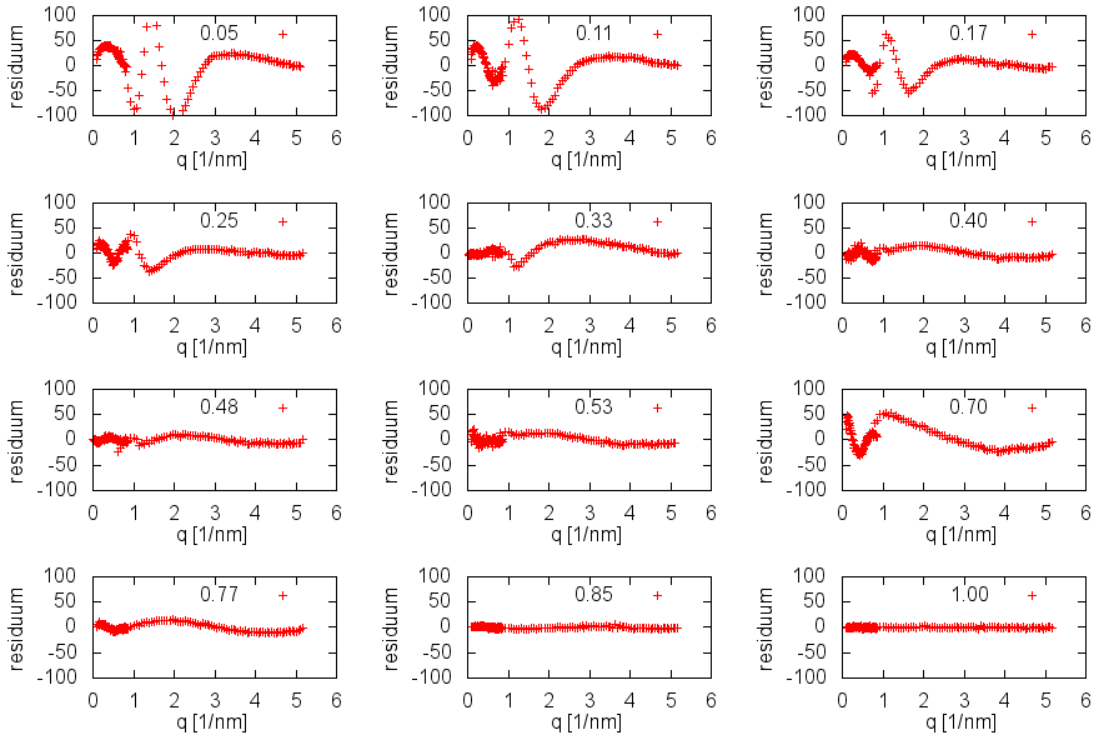

Figure S4: Residuals for the TS fits shown in Figure S3. Residuals are calculated as $Res = \frac{I_i - I_{i,fit}}{\Delta I_i}$ with the measured Intensity I_i, its error ΔI_i and the fitted value $I_{i,fit}$.

Table S2: Parameter for the TS fits shown in Figure S3 and calculated values for $\langle \eta^2 \rangle$.

	fit parameter SASfit				calculated $\langle \eta^2 \rangle / cm^{-1} nm^{-3}$		
x_{MRTIL}	ξ/nm	D_s/nm	$\langle \eta^2 \rangle / cm^{-1} nm^{-3}$	backgr./cm^{-1}	case 1	case 2	case 3
0.05	2.05	5.44	0.6600	0.3500	0.9161	0.6726	0.0709
0.11	1.90	6.53	0.6799	0.3669	0.9259	0.6859	0.1037
0.17	2.29	7.48	0.6595	0.4313	0.9297	0.6926	0.1317
0.25	2.28	8.59	0.6581	0.4851	0.9191	0.6862	0.1509
0.33	2.29	10.76	0.6468	0.5359	0.8936	0.6644	0.1570
0.40	2.30	13.39	0.6186	0.5657	0.8537	0.6292	0.1523
0.48	1.86	27.36	0.6012	0.5881	0.7975	0.5776	0.1361
0.53	1.96	60.00	0.5508	0.5981	0.7493	0.5336	0.1203
0.70	1.74	60.00	0.3230	0.6352	0.5466	0.3488	0.0511
0.77	1.14	60.00	0.2555	0.5951	0.4509	0.2641	0.0252
0.85	0.35	6.00	0.3359	0.5757	0.3059	0.1428	0.0019
1.00	0.65	5.64	0.2400	0.6000	0.0000	0.0121	0.0687

Core-shell Model

Additionally to the TS model a model assuming spherical particles with a core-shell structure was fitted to all SANS data. The scattering length densities ρ_c, ρ_{sh} and ρ_s for the core, shell and solvent, respectively, were calculated assuming a MRTIL phase composed of bmim[$FeCl_4$] and the surfactant headgroup, and a shell composed of the surfactant tail, decanol and oil. The oil portion in the interface was calculated such that theoretical (INV_t) and measured (INV_m) invariants were identical. INV_m was calculated from the measured intensity I(q) with the help of SASfit,[3] $\rho_{c,sh,s}$ and $\Phi_{c,sh,s}$ were calculated as described above:

$$INV_m = \int_0^\infty q^2 I(q) dq \tag{S4a}$$

$$INV_t = \pi^2(\Phi_c\Phi_{sh}\Delta\rho_{c,sh} + \Phi_c\Phi_s\Delta\rho_{c,s} + \Phi_{sh}\Phi_s\Delta\rho_{sh,s}) \tag{S4b}$$

For samples of $x_{MRTIL} < 0.4$ the core was assumed to be composed by the MRTIL-phase, for samples with $x_{MRTIL} \geq 0.4$ by the oil phase. For the sample with $x_{MRTIL} = 1.00$ the shell radius was set to $dR = 0$ and ρ_c was calculated as composed by surfactant tail and alcohol due to an absence of cyclohexane in this sample. The scattering intensity of the used model can be expressed as a product of a form factor P and a structure factor S:

$$I(q) = N \cdot P(q, R_c, \delta R) \cdot S(q, R_{HS}, \Phi_p) \tag{S5}$$

The polydisperse form factor is given by a model characterized by a core with radius R_c and a shell with thickness δR.

$$P(q,R_c,\delta R) = [K(q,R_c,\delta R) - K'(q,R_c)]^2 \tag{S6a}$$

$$K(q,R_c,\delta R) = \frac{4}{3}\pi(R_c+\delta R)^3(\rho_{sh}-\rho_s)3\frac{\sin q(R_c+\delta R) - q(R_c+\delta R)\cos q(R_c+\delta R)}{(q(R_c+\delta R))^3} \tag{S6b}$$

$$K'(q,R_c) = \frac{4}{3}\pi R_c^3(\rho_c-\rho_{sh})3\frac{\sin qR_c - qR_c\cos qR_c}{(qR_c)^3} \tag{S6c}$$

where R_c is expressed by the lognormal distribution:

$$LogNorm(R,\mu,\sigma) = \frac{N}{\sqrt{2\pi}\sigma R}\exp(-\frac{\ln(R/\mu)^2}{2\sigma^2}) \tag{S7}$$

The n^{th} moment $\langle R^n\rangle$ of the core radius can be calculated as

$$\langle R^n\rangle = \mu^n \exp\frac{1}{2}\sigma^2 n^2 \tag{S8}$$

The polydispersity index p is defined as

$$p = \frac{\langle R^2\rangle}{\langle R\rangle^2} - 1 \tag{S9}$$

$S(q,R_{HS},\Phi_p)$ is given by the structure factor of a hard sphere.[4] Figure S5 and Figure S6 show fits and residuals, respectively. In general, the residuals for the core-shell model are rather small (different scale compared to Figure S4). However, it is interesting to note that upon approaching the bicontinuous phase from the oil-rich side one observes relatively large deviations just before and after entering the bicontinuous range. This might be an indication that here already before becoming bicontinuous the droplet picture is not so good anymore, as one may observe percolation already for lower content of MRTIL. That one has a rather broad structural transition with a wide percolation range is already evidenced from the conductivity data (Figure 3) which show a rather slow increase of conductivity and no sharp upturn.

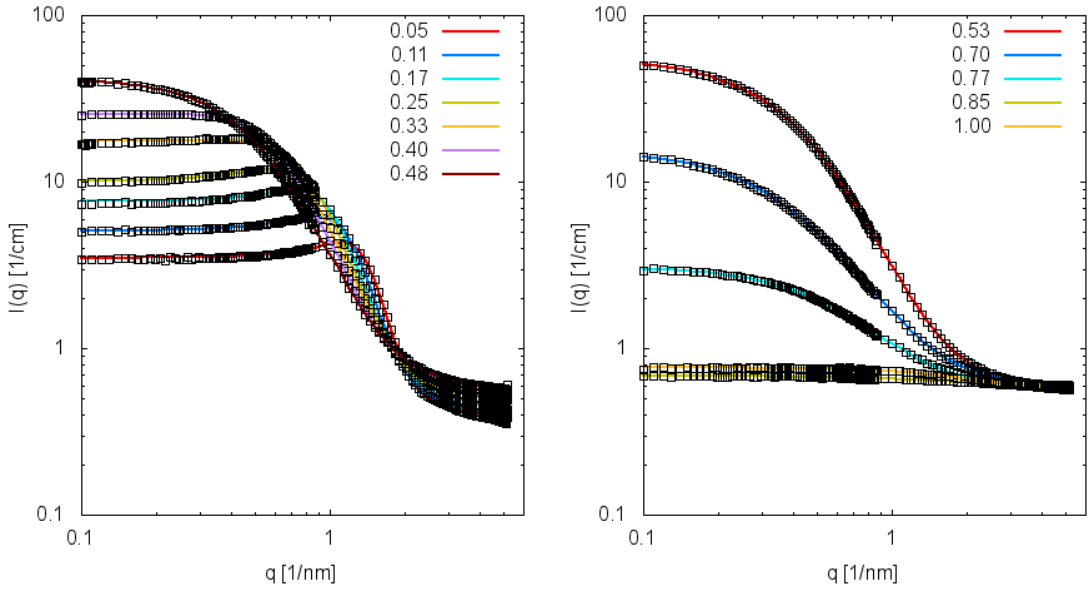

Figure S5: SANS curves performed with D12-cyclohexane as the oil phase. The samples are along the experimental path shown in Figure 1. Ratios between MRTIL and oil are x_{MRTIL}=0.05-0.48 (left) and x_{MRTIL}=0.53-1.00 (right). Lines are fits with the core shell model.

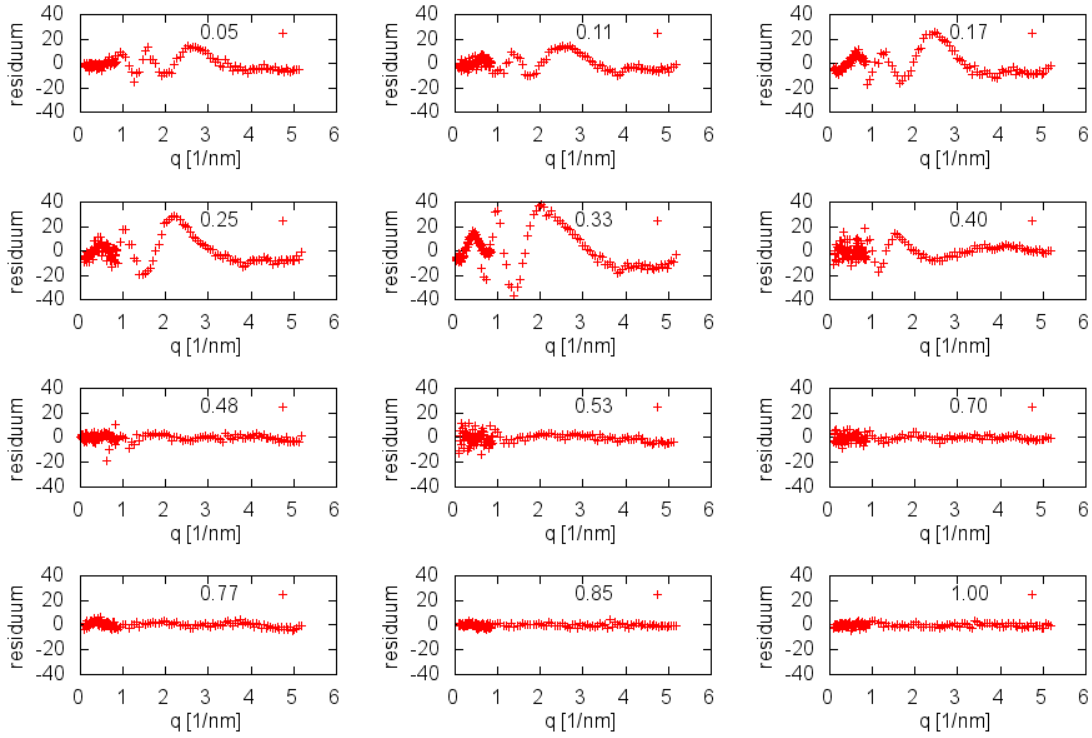

Figure S6: Residuals for the core-shell fits shown in Figure S5, Residuals are calculated as described in Figure S4.

Table S3: Parameters for fits with the core-shell model. Values for the scattering length densities $\rho_{c,sh,s}$ are precalculated and not variables during the fit procedure.

x_{MRTIL}	N	σ	μ	$\frac{\delta R}{nm}$	$\frac{\rho_c}{nm^{-2}}$	$\frac{\rho_{sh}}{nm^{-2}}$	$\frac{\rho_s}{nm^{-2}}$	$\frac{R_{HS}}{nm}$	Φ_p
0.05	76463.2	0.36	0.94	0.58	0.00019556	0.0000042	0.0006680	2.11	0.22
0.11	62275.0	0.36	1.00	0.57	0.00017956	0.0000123	0.0006680	2.46	0.18
0.17	50567.7	0.39	1.05	0.58	0.00017179	0.0000012	0.0006680	2.87	0.16
0.25	45848.3	0.37	1.22	0.45	0.00016745	0.0000047	0.0006680	3.37	0.14
0.33	42004.4	0.44	1.17	0.43	0.00016483	-0.0000092	0.0006680	3.98	0.11
0.40	15906.1	0.30	2.44	0.95	0.00016316	0.0000009	0.0006680	4.92	0.06
0.48	18666.1	0.38	2.03	0.97	0.00016197	0.0000164	0.0006680	6.16	0.02
0.53	18438.7	0.43	1.83	1.07	0.00016131	0.0000425	0.0006680	6.01	0.01
0.70	39703.5	0.44	1.79	2.18	0.00015988	0.0001139	0.0006680	1.03	0.27
0.77	52876.0	0.43	1.13	1.36	0.00015950	0.0001463	0.0006680	0.94	0.20
0.85	875261.0	0.46	0.32	1.03	0.00015907	0.0001327	0.0006680	–	–
1.00	331791.0	0.23	0.82	–	-0.00003300	–	0.0001580	–	–

References

(1) Teubner, M.; Strey, R. *J. Chem. Phys.* **1987**, *87*, 3195–3200.

(2) Sears, V. F. *Neutron News* **1992**, *3*, 26–37.

(3) Kohlbrecher, J.; Bressler, I. http://kur.web.psi.ch/sans1/SANSSoft/sasfit.html.

(4) Ashcroft, N. W.; Lekner, J. *Phys. Rev.* **1966**, *145*, 83–90.