Widening the View on Dispersant-Pigment Interactions in Colloidal Dispersions with Saturation Transfer Difference NMR Spectroscopy

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Supporting Information

Contents:

1. Details concerning Pigment Red 122

Scheme S1: Chemical structure of PR122 quinacridone pigment. Both quinacridone type molecules occur in a 3:1 ratio.

Figure S1: SEM images of PR122 powder.

The average dimension of PR122 particles was obtained from analysis of the dimensions of the individual pigment particulates using SEM images and found to correspond to 10 by 30 by 100 nm on average.

2. ^{1}H NMR spectra of the SDS:PR122 dispersions used for STD NMR analysis
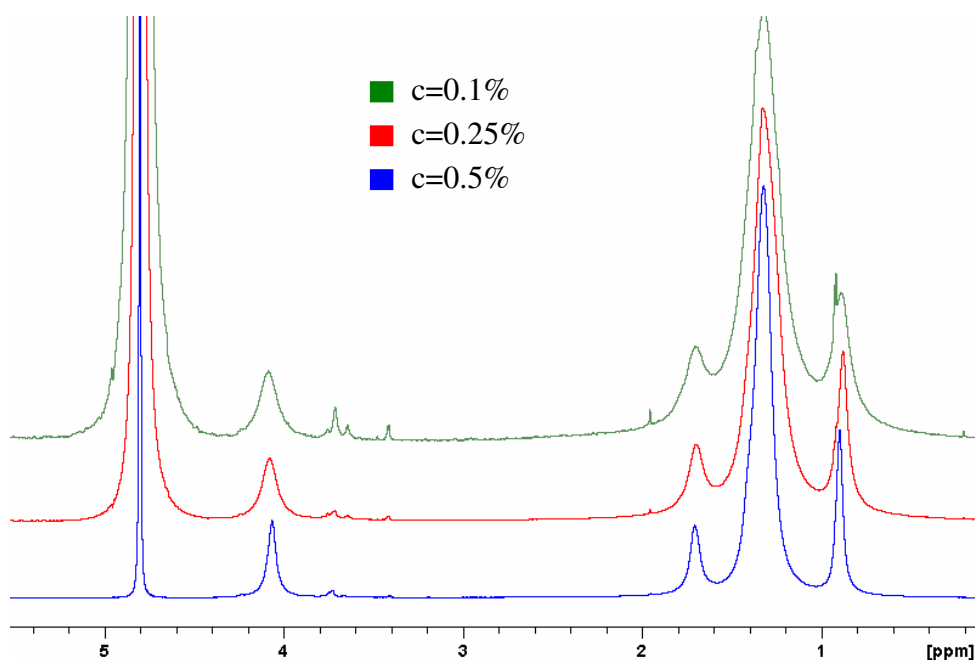
Figure S2: ^{1}H NMR spectra of SDS-PR122 dispersions containing 0.25%w/w pigment presented as a function of SDS concentration and representing the samples used for the STD analysis (Figure 2 main text). The sharpening of the resonance line width as the SDS concentration increases is noticeable and indicative of line broadening resulting from the intermolecular association with the pigment surface. Spectra are scaled to yield the same height for the α-CH$_2$ resonance.

2. ^{1}H NMR spectra of the SDS:PR122 dispersions used for STD NMR analysis
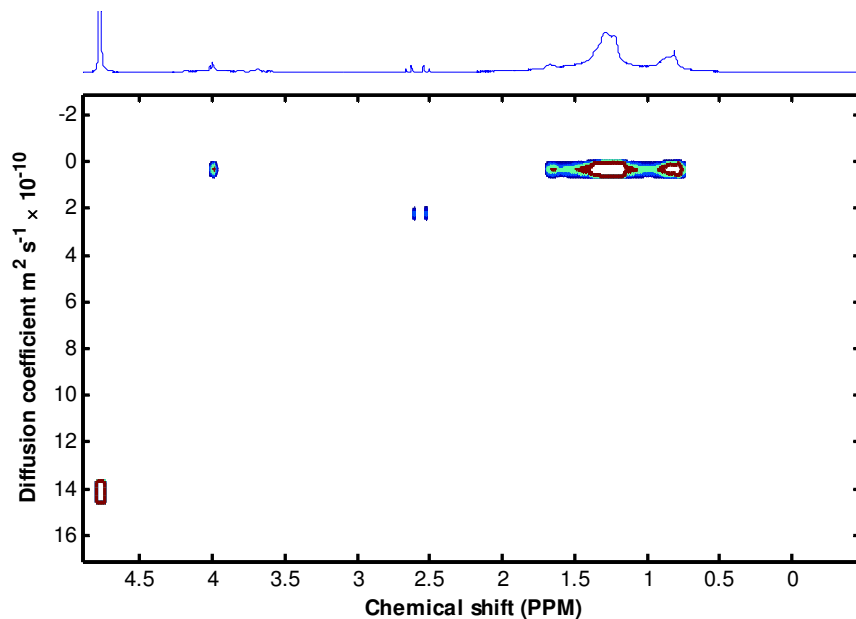

Figure S3: DOSY spectrum of the 6%/5% (w/w) SDS-PR122 dispersion. The spectrum was recorded using the standard BPPSTE pulse sequence. [Ref. 1S] The gradient pulse duration δ and diffusion delay Δ were 1.5ms and 0.7s respectively. The data was processed using the DOSYToolbox developed by Nilsson et al. [Ref. 2S]. The apparent diffusion coefficient of $2.6 \times 10^{11} m^2 s^{-1}$ extracted from this spectrum compares favorably to that of SDS micelles, found to be $2.8 \times 10^{11} m^2 s^{-1}$. Due to the important line broadening, no experimental Δ/δ conditions could be defined that afforded the signal decay for the broadened resonances to be monitored.

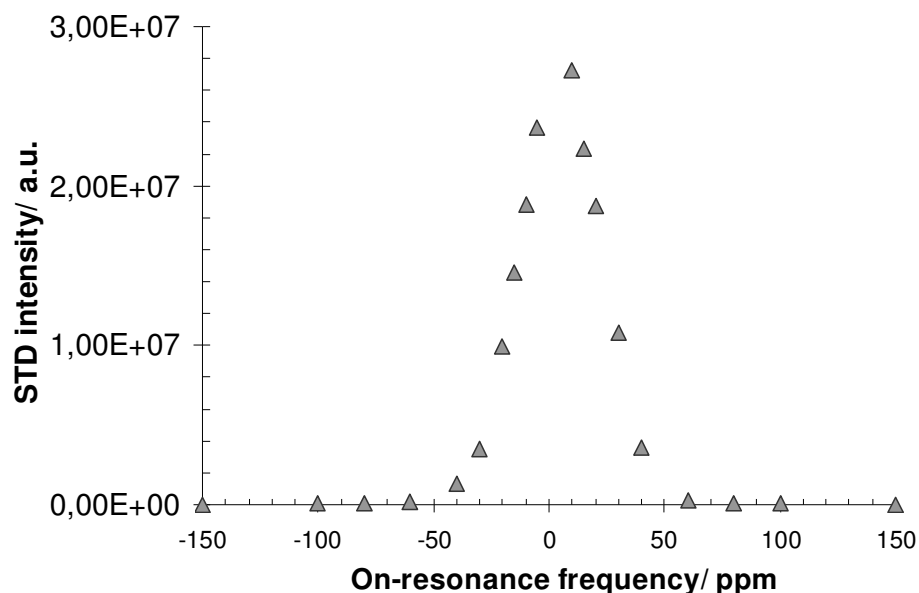## 3. Variation of the off-resonance frequency

Figure S4: Saturation transfer difference intensity profiles for a 0.25/0.25% (w/w) SDS-PR122 dispersion.

The procedure used was similar to the one devised by Rademacher et al. [Ref 3S]. STD experiments were acquired with the off-resonance frequency set to 300ppm and variable on-resonance frequencies between -150 and +150 ppm in steps of varying size. Zero intensity results when the pigment is not saturated. When the pigment resonance envelope is reached, non zero STD intensity is observed for SDS. As the pigment envelope is scanned through, the intensity evolves as shown above. Datapoints between 10 and -5 ppm were excluded from the analysis, to avoid contributions from saturated SDS ligand to contribute to the STD intensity.

Only the STD intensity profile of the main chain methylene resonance is shown, however, a similar profile was obtained when analyzing any other SDS resonance.

The STD intensity plot reveals that the on-resonance frequency approximately covers the region between 60 and –60 ppm. An apparent line-width of 28.7 ± 6.2 kHz at half height was found for this excitation profile by fitting a Gaussian function to the data, as shown below.
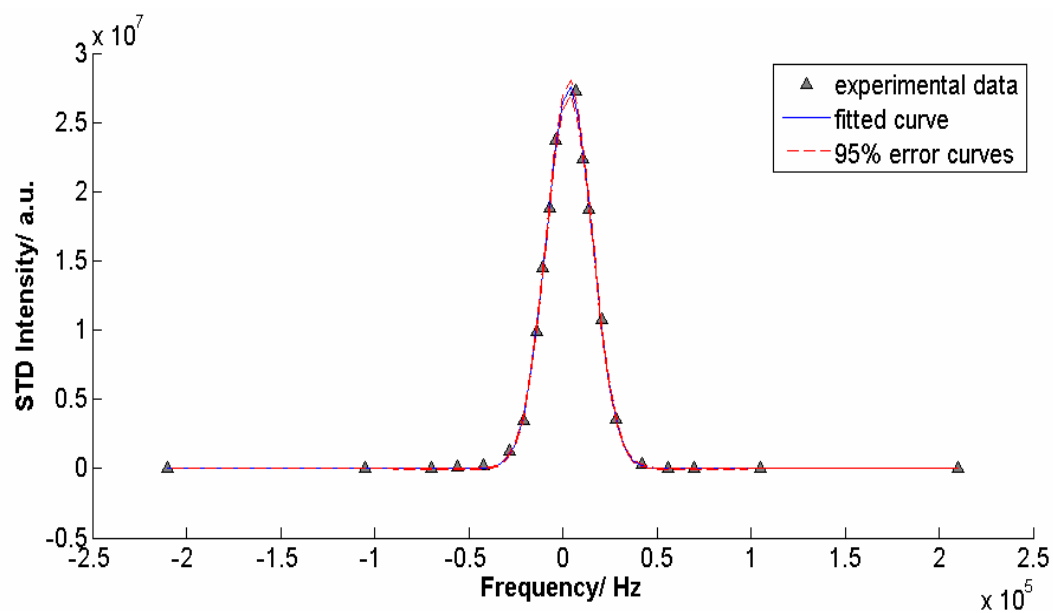
Figure S5: Saturation transfer difference intensity profiles for a 0.25/0.25% (w/w) SDS-PR122 dispersion

5. Experimental details

Materials:

Pigment Red 122 (2, 9-dimethylquinacridone) was bought from Clariant. Sodium Dodecylsulfate (Texapon K12 P) was bought from Cognis Deutschland GmbH and used as received. Poly-ε-caprolactone-δ-valerolactone octyl terminated oligomer was synthesized using standard procedures and provided as such by AGFA Materials N.V. Deuterium oxide (99.9% isotopic purity) was bought from Aldrich. Acetone–d6 (99.5% isotopic purity) was bought from ACROS Organics.

Dispersion preparation

All SDS–PR122 dispersions in D_2O as well as oligomer-PR122 in acetone were prepared by the wet-milling procedure, wherein the pigment and SDS are mixed in D_2O and subsequently ground in the presence of yttrium-stabilized zirconium oxide beads (Tosoh Co, 0.4mm diameter) over 72 hours. Afterwards, the beads are filtered away and the obtained dispersions are stored under ambient conditions.

NMR measurements

All spectra were recorded on a Bruker Avance II 700 spectrometer, operating at 700.13 MHz for the ^{1}H NMR frequency and equipped with a ^{1}H, ^{13}C, ^{15}N TXI-Z gradient probe. The temperature in all measurements was set to 298 K and controlled to within 0.05K by way of a Eurotherm 3000 controller. Topspin 2.1 was used for all acquisition and processing.

Typically, 1D spectra were recorded using a spectral width of 15ppm. 32K datapoints were sampled for an acquisition time of 1s with a relaxation delay of 20s. STD measurements were obtained using the standard pseudo2D version of the STD NMR pulse sequence (stddiff) wherein on and off resonance spectra are recorded in an interleaved manner. Following optimization of the off-resonance frequency, all STD spectra were recorded with on and off-resonance frequency of 20 and 300ppm, respectively. The number of scans was adjusted to obtain a satisfactory signal to noise ratio and typically ranged between 16 and 64. No water suppression was applied. The saturation was performed via a cascade of 720° Gaussian pulses with a length of 50ms and an interpulse delay of 1 ms. The total duration of the

saturation sequence was varied from 0.02-5s to obtain the STD intensity buildup. Linear regression to the initial buildup rates was limited to the first 600 ms, i.e. well below the smallest T_1 value observed for the SDS resonances in the various samples. The T_1 values were obtained using the standard inversion recovery sequence followed by single exponential fitting. To allow for complete relaxation of pigment and ligand, a relaxation delay of 20s was used throughout. For the experiments with the octyl-terminated poly-ε-caprolactone-δ-valerolactone a saturation time of 30s was used, with otherwise similar set up as for the SDS-PR122 dispersions.

Prior to Fourier transformation the data was multiplied with an exponential function with a 3 Hz line broadening factor prior to Fourier transformation. Baseline correction was applied using the polynomial baseline correction within the TopSpin 2.1 software.

For negative controls we acquired STD spectra of each of dispersant without the pigment, using the same experimental setup as for dispersion studies. No STD response was noted in either of the control experiments.

6. T_1 relaxation determination of free and bound SDS

Concentration [%]	T_1 SDS solution [s]				T_1 SDS-PR122 dispersion [s]			
	α-CH$_2$	β-CH$_2$	-(CH$_2$)$_9$	CH$_3$	α-CH$_2$	β-CH$_2$	-(CH$_2$)$_9$	CH$_3$
0.1	1.40	1.08	1.05	2.49	1.67	1.37	1.43	1.36
0.175	1.3	1.02	1.04	2.23	1.45	1.27	1.28	1.30
0.2	1.28	1.01	1.03	2.27	1.18	1.21	1.22	1.26
0.3	1.14	0.89	0.89	1.76	1.03	1.04	1.05	1.12
0.4	1.10	0.85	0.83	1.61	0.99	0.96	0.98	1.10

Table S1: T_1 relaxation characteristics of SDS in solution and in the various SDS-PR122 dispersions.

The T_1 relaxation data were measured using the standard 1D inversion recovery pulse sequence. For SDS in solution without pigment solutions are above CMC starting at 0.3% (w/w), as reflected by the characteristic change to the T_1 values of the methyl and aliphatic chain methylene groups. Values obtained on the various dispersions with 0.25% w/w PR122 indicate clearly different values for the same concentration of SDS in the absence of the pigment. Due to the fast exchange with respect to the relaxation time scales, these values represent population averages of the free and bound T_1 values. Using a procedure previously described by Choudhury et al. [Ref. 4S], the value of T_1 for SDS bound to the pigment surface, was obtained by plotting $(T_1)^{-1}$ with respect to the SDS concentration and linearly extrapolating the curve to zero SDS concentration, thereby assuming that at infinitely low SDS concentration all SDS is bound and no free SDS is present. This is shown for the $-(CH_2)_9-$ resonance of SDS in the graph below.

The T_1 values obtained in this fashion are: 2.1s (α-methylene), 1.6s (β-methylene), 1.7s (alkyl chain protons), 1.5s (methyl protons).

The longest T_1 value being 2.1s, the use of a relaxation delay prior to saturation of at least 20s should be sufficient to avoid any artifacts due to incomplete relaxation.
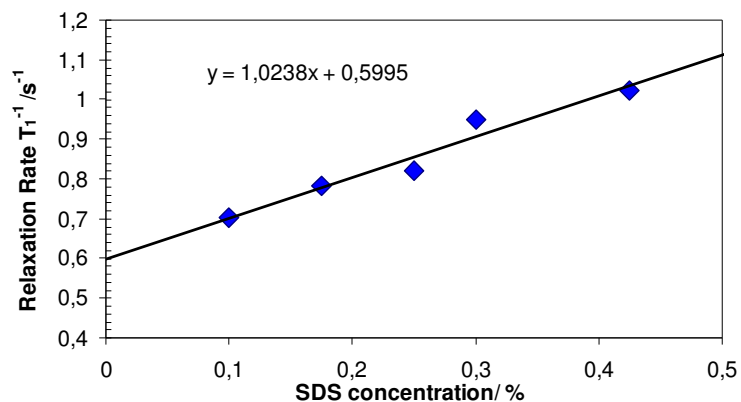
Figure S6: Spin-lattice relaxation rate determined for the main alkyl chain at different SDS concentrations. Diamonds represent experimental values; a solid line shows a linear extrapolation of the low concentration region to c=0, using the procedure described in [Ref 4S].

7. STD response as a function of the SDS concentration in SDS-PR122 dispersions

Concentration [%]	α-methylene	β-methylene	-$(CH_2)_9$-	methyl protons
0.1	0.327	0.323	0.320	0.323
0.175	0.226	0.223	0.224	0.238
0.3	0.152	0.153	0.156	0.178
0.4	0.118	0.120	0.124	0.142
0.5	0.095	0.095	0.100	0.120

Table S2: Values of the initial slopes representing the dependence of the STD response, obtained for individual SDS resonances as a function of dispersant concentration (in all cases, the error on the slope is not larger than 0.005)
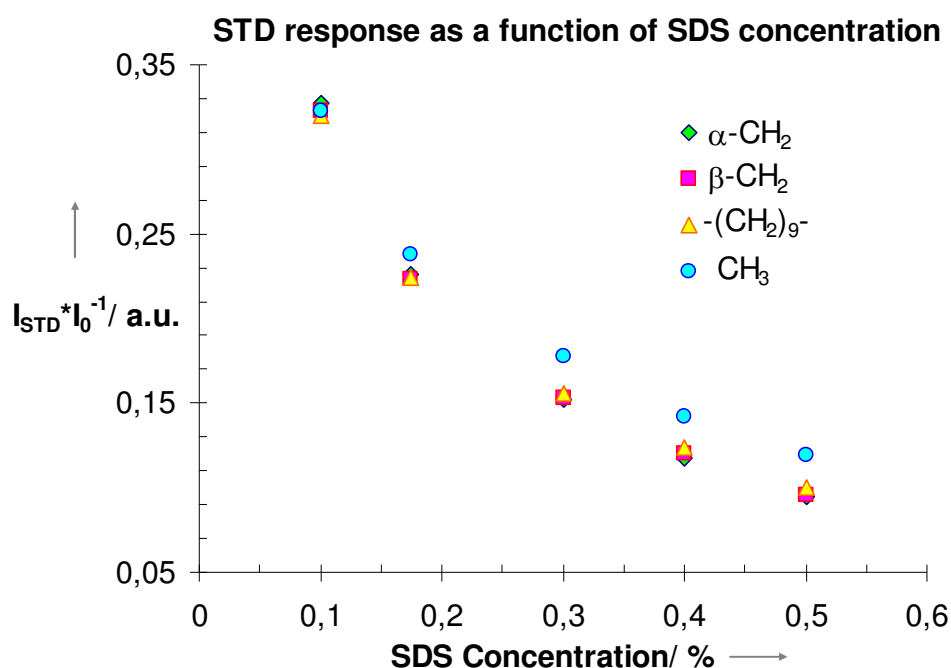

Figure S7: Graphical representation of the data in Table S2. This graph is converted into Figure 2 (main text) when the individual values are multiplied by the SDS dispersion weight percent.

8. Control experiments

a) Demonstration of the presence of micellar SDS resonances via removing the surface associated SDS contribution through T_2 relaxation filtering.
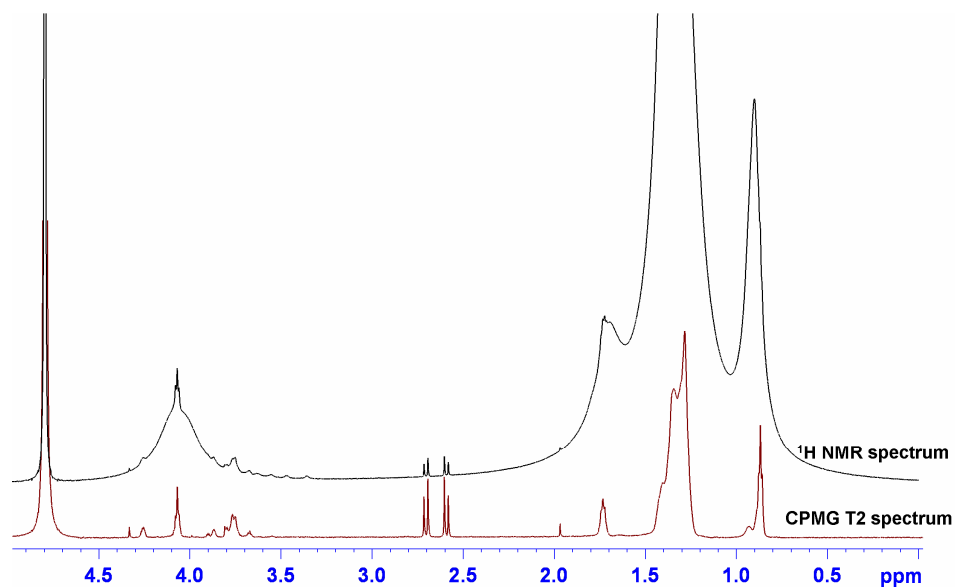

Figure S7: 1D CPMG NMR spectrum recorded for the SDS:PR122 (7/5 w:w%) dispersions with 50 ms total CPMG time. The experiment clearly uncovers the sharp resonances assigned to micellar SDS by removing the surface associated SDS contribution through T2 relaxation filtering. The resulting spectrum corresponds well to that of SDS in solution (see Figure S8 top spectrum), except for the alkyl chain region where the residual of the broadened signal is still large enough to prevent a clear view on the alkyl chain resonance of the micellar form. Signals in the neighborhood of alfa methylene correspond to impurities present in the commercial SDS and do not have an impact on STD results, since they do not generate a STD response.

b) STD NMR control experiment in the absence of the pigment

Control STD NMR experiment was performed for SDS solution (10% = 41*cmc) to exclude the possibility of direct irradiation of SDS micelles. All parameters in the control experiment were maintained as in dispersion studies; the saturation time of 2s was applied.

No STD response of the SDS resonances was observed when the on-resonance irradiation was applied at 30, 20 and 10ppm. In fact, only a direct irradiation of the SDS resonances resulted in a visible STD response.
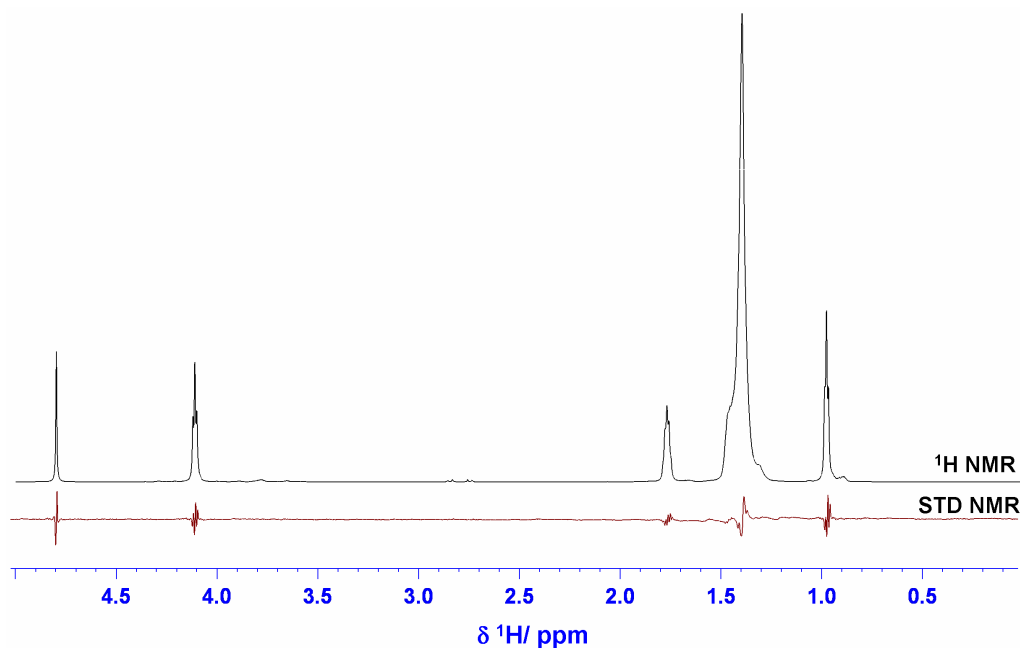

Figure S8: Reference ^{1}H NMR (top) and corresponding STD NMR spectrum (bottom) of SDS solution in D_2O (10% w/w), resulting for on-resonance irradiation of 2s at 30ppm. The STD spectrum is scaled 100:1 in respect to its original size in order to demonstrate that only the subtraction artifacts may be found

References:

[1S] Wu, D. H.; Chen, A.; Johnson, C. S. *J. Magn. Reson.A,* **1995,** *115*, 123.

[2S] Nilsson, M.; Connell, M.A.; Davis, A.L.; Morris, G.A. *Anal. Chem.* **2006**, *78*, 3040-3045.

[3S] Rademacher, C.; Rama Krishna, N.; Palcic, M.; Parra, F.; Peters, T. *J. Am. Chem. Soc.* **2008**, *130*(11), 3669-3675.

[4S] Choudhury, R. P.; Schoenhoff, M. *J.Chem.Phys*. **2007**, *127*, 234702.