

Electronic Supplementary Information

Dye Exchange in Micellar Solutions. Quantitative Analysis of Bulk and Single Molecule Fluorescence Titrations.

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Contents

ADDITIONAL DATA.....	2
Direct TX100 UV-Absorption	2
R123 in TX100 micelles.....	2
C460 in TX100 micelles.....	3
C152 in TX100 micelles.....	3
Comparison of several dyes in exchange with TX-100.....	4
Fluorescence Correlation Spectroscopy data of R123 and C152	4
Experimental Section	5
FCS Measurements.....	5
References.....	5
Fitting functions	6
Concentration Model	6
APNModel_S1	6
Derived Properties	7
APNModel_DyeExchangeFluorFull.....	7
APNModel_DyeExchangeFluorShort.....	7
APNModel_AbsorptionBandRatio.....	8
APNModel_DyeExchangeFCS_tauDMean.....	9
Other models used before:	9
APNModel_Conductivity	9
APNModel_Conductivity_k1	10
APNModel_Conductivity_k2	10
APNModel_MolarConductivity	10
APNModel_SelfDiffusion.....	11
APNModel_NMRChemicalShifts	11
APNModel_SurfaceTensionSzyszkowski	12
Utility functions.....	13
APNModel_d2S1	13
APNModel_d2S1	13

References to figures and equations refer to the main paper.

ADDITIONAL DATA

Direct TX100 UV-Absorption

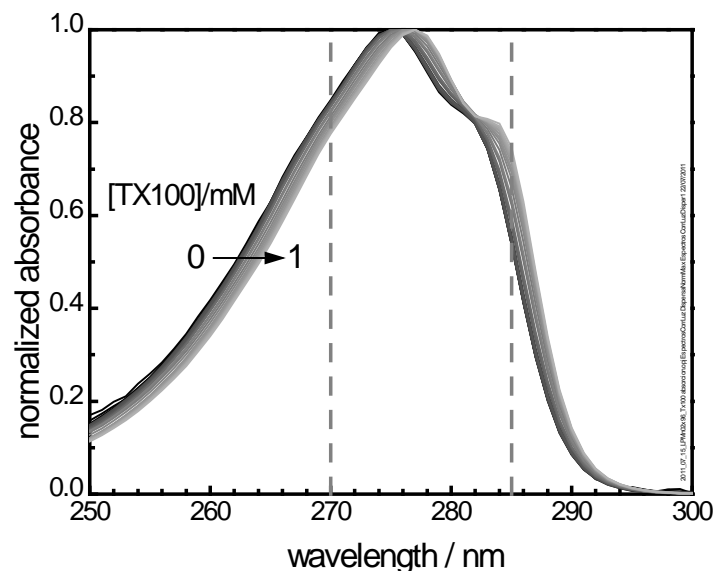


Figure S11: Corrected absorption spectra of TX100 normalized at the maximum with concentrations between 0 and 1 mM. Dashed lines indicate the wavelength used for the ratiometric analysis.

R123 in TX100 micelles

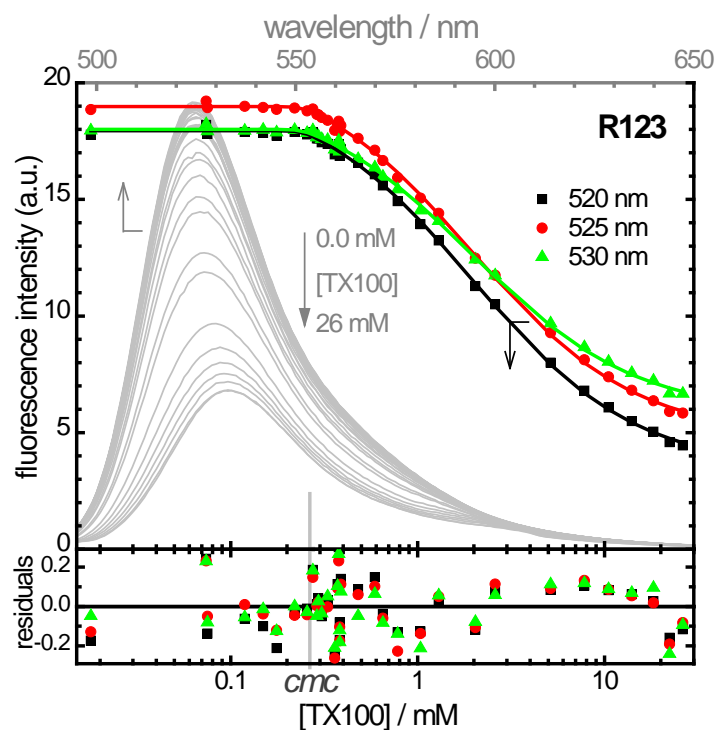


Figure S12: Fluorescence of R123 in aqueous TX-100 solutions with $[TX-100]= 0-26$ mM. Grey curves and upper wavelength scale: fluorescence spectra. Filled symbols and lower concentration scale: Fluorescence intensities at three wavelength vs. TX-100 concentration. Continuous curves: global fit of equations (4-7, 16) at three wavelengths with $cmc=0.24\pm 0.01$ mM, $r=0.1\pm 0.1$, $K = (65.5\pm 1) 10^3$ M⁻¹ and a ratio $F_b/F_f = 0.25$ at 525 nm ($\lambda_{exc}=488$ nm, $[R123]_0 = 2 \cdot 10^{-8}$ M).

C460 in TX100 micelles

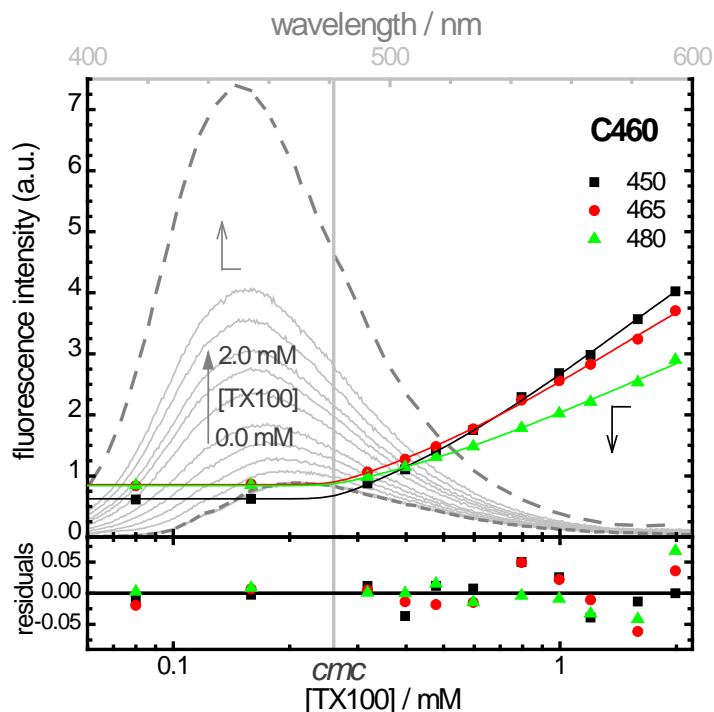


Figure S13: Fluorescence of C460 in aqueous TX-100 solutions with [TX-100]= 0-2 mM. Grey curves and upper wavelength scale: fluorescence spectra and pure emission spectra of free C460 (short dash) and bound C460 (dash). Filled symbols and lower concentration scale: Fluorescence intensities at three wavelength vs. TX-100 concentration. Continuous curves: global fit of equations (4-7, 16) at three wavelengths with $cmc=0.25\pm 0.01$ mM, $r=0.1$ (fix), $K = (82\pm 5) 10^3 \text{ M}^{-1}$ and a ratio $F_b/F_f = 12$ at 450 nm ($\lambda_{exc}=380\text{nm}$, $[C460]_0 = 3 \cdot 10^{-7} \text{ M}$).

C152 in TX100 micelles

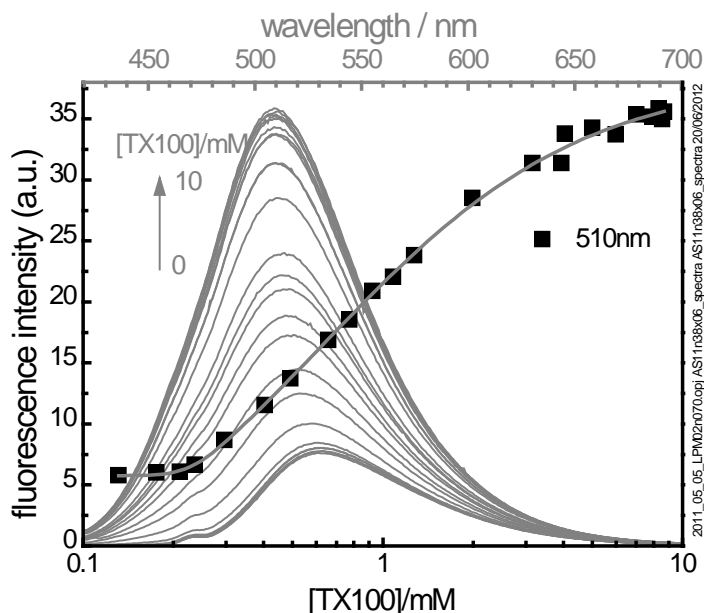


Figure S14: Fluorescence of C152 in aqueous TX-100 solutions with [TX-100]=0-10 mM. Grey curves and upper wavelength scale: fluorescence spectra. Black squares and lower concentration scale: Fluorescence intensities at 510 nm vs. TX-100 concentration. Solid grey curve: fit of eqs. (4-7, 16) with $cmc = 0.22\pm 0.02$ mM, $r = 0.18\pm 0.13$, $K = (170\pm 10) 10^3 \text{ M}^{-1}$ at 510 nm. ($\lambda_{exc}=380\text{nm}$, $[C152]_0 < 5 \cdot 10^{-7} \text{ M}$)

Comparison of several dyes in exchange with TX-100

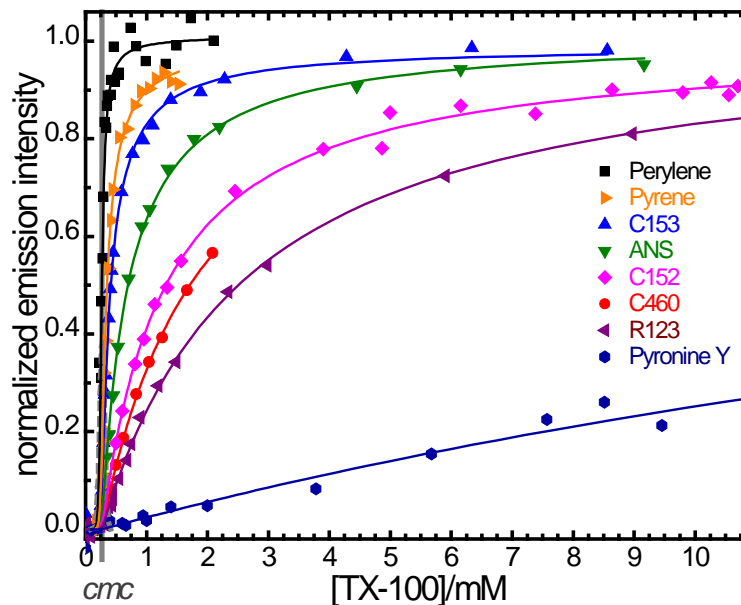


Figure S15: Normalized fluorescence emission intensity $F_{norm} = (F - F_f) / (F_b - F_f)$ of several dyes in aqueous solutions of TX-100 as function of surfactant concentration. Continuous curves are results of a global fit of equations (4-7, 16) with fixed values of $cmc=0.27$ mM and $r=0.15$. The excitation and emission wavelength and the ratios F_b / F_f are given in Table 1.

Fluorescence Correlation Spectroscopy data of R123 and C152

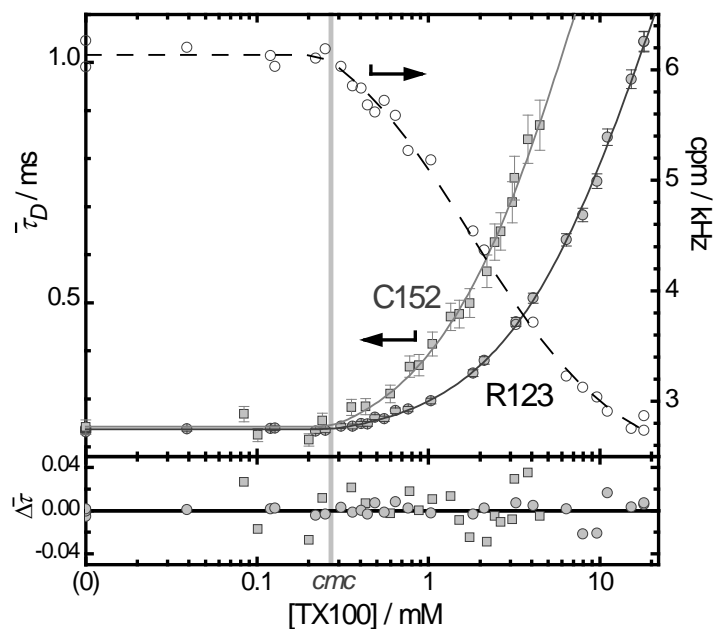


Figure S16: Mean diffusion times $\bar{\tau}$ (filled symbols) and fluorescence counts per second and molecule (cpm , open circles) from FCS titrations of R123 (circles) and C152 (squares) in TX100 solutions with $[TX100]=0-18$ mM. Continuous lines are fits of eq. (23) to $\bar{\tau}$ and (16) to cpm , both with eqs. (4-7) for the micelle concentration. The fit parameters are given in Table 2 and in the text.

Experimental Section

FCS Measurements

The confocal epi-illuminated setup used for the FCS measurements is home-built^{1,2} and similar to that described elsewhere.^{3,4} A drop of each sample was deposited on a borosilicate coverslip (Menzel Gläser, NO. 1 DE) or in a well of a glass bottom microplate (Whatman Ltd.). The samples were excited by the continuous linearly polarized light of a laser diode (Becker&Hickl, BDL-485-SMC (489 nm) or BDL-405-SMC (405nm), DE) coupled to a monomode optical fiber (Point-Source, kineFLEX-P-1-S-405-0.7, UK). The light output of the fiber was collimated (Schäfter&Kirchhoff, 60FC-4-6,2-01-DI, DE), spectrally cleaned (Semrock, Brightline HC 482/18 or Maxdiode LD01-405/10, US), redirected by a dichroic mirror (Semrock, Brightline BS R488, US or AHF Analysentechnik, z405 RDC, DE) and focused into the sample by a high aperture microscope objective (Olympus, UPLSAPO 60xW/1.20, water immersion) mounted in an inverted microscope (Olympus, IX-71). The fluorescence was collected by the same objective and then refocused through the dichroic mirror onto a pinhole (Thorlabs, Ø=100 µm, US) in the image plane. The light passing the pinhole was collimated, then split into two beams by a nonpolarizing beamsplitter cube (Thorlabs, BS016, US) and each beam focused onto avalanche photodiodes (MPD50CTC APD, Ø=50 µm, MPD, Italy). Band-pass filters (Semrock, Brightline HC 525/45, US or AHF Analysentechnik, HQ550/100M, Germany) in front of the detectors discriminated fluorescence from scattered laser light. The output signals were processed and stored by TCSPC-modules (SPC 132, Becker & Hickl GmbH, Berlin, Germany). Correlation curves were calculated with the Single Photon Counting software by Becker & Hickl GmbH.

Typically 10 million photons were collected for each correlation curve. All measurements were made at stabilized temperature, 25.0±0.5°C. The excitation power as measured in the focus of the microscope objective (power meter Thorlabs, PM30-120, US) was typically P=120 µW, corresponding to a mean irradiance of $I_0/2 = P/(\pi \cdot w_{xy}^2) = 9 \text{ kW cm}^{-2}$.⁵

The focal area and the detection volume were calibrated at 489 nm with Rhodamine 123 and at 405 nm with C152. The diffusion coefficient $D(\text{R123}, 25^\circ\text{C}) = (4.6 \pm 0.4) \times 10^{-10} \text{ m}^2\text{s}^{-1}$ was estimated from PFG-NMR⁶ and dual-focus FCS⁷ data.⁸ The diffusion coefficient $D(\text{C152}, 25^\circ\text{C}) = (5.2 \pm 0.6) \times 10^{-10} \text{ m}^2\text{s}^{-1}$ has been taken from Bordello et. al.¹ The diffusion coefficients are given for 25°C.

References

- 1 J. Bordello, M. Novo and W. Al-Soufi, *J. Colloid Interface Sci.*, 2010, **345**, 369-376.
- 2 D. Granadero, J. Bordello, M. J. Pérez-Alvite, M. Novo and W. Al-Soufi, *Int. J. Mol. Sci.*, 2010, **11**, 173-188.
- 3 S. Felekyan, R. Kuhnemuth, V. Kudryavtsev, C. Sandhagen, W. Becker and C. A. M. Seidel, *Rev. Sci. Instrum.*, 2005, **76**.
- 4 W. Al-Soufi, B. Reija, M. Novo, S. Felekyan, R. Kühnemuth and C. A. M. Seidel, *J. Am. Chem. Soc.*, 2005, **127**, 8775-8784.
- 5 C. Eggeling, J. Widengren, R. Rigler and C. A. M. Seidel, *Anal. Chem.*, 1998, **70**, 2651-2659.
- 6 P. O. Gendron, F. Avaltroni and K. J. Wilkinson, *J. Fluoresc.*, 2008, **18**, 1093-1101.
- 7 C. Muller, A. Loman, V. Pacheco, F. Koberling, D. Willbold and W. Richtering, *Europhys. Lett.*, 2008, **83**.
- 8 P. Kapusta, , *Absolute Diffusion Coefficients: Compilation of Reference Data for FCS Calibration*, http://www.picoquant.com/technotes/appnote_diffusion_coefficients.pdf.

Fitting functions

We provide ready to use fitting functions for Origin Data Analysis Software (OriginLab Corporation, Northampton, MA 01060, USA) as compressed zip-archive. Updated versions can be downloaded from the author's webpage.

The functions were tested with Origin 8.5 SR1.

For use in Origin the zip-archive should be decompressed in a temporal directory and the functions should be added from the *fitting function organizer* to the Origin Fitting functions. (Do not copy them directly to the Origin directory.) We propose to add them to a new category such as "APNModel".

All functions can be used for nonlinear fitting and for calculations in columns or other functions. For calculations the functions should be called as "nlf_FunctionName(parameters)", for example: "nlf_APNModel_S1(cS0,cmc,r)".

The functions also serve as examples for other data analysis packages. Therefore we describe briefly the main code of each of the functions.

For further information see:

Wajih Al-Soufi, Lucas Piñeiro, Mercedes Novo, *A model for monomer and micellar concentrations in surfactant solutions: Application to conductivity, NMR, diffusion, and surface tension data*, **Journal of Colloid and Interface Science**, Volume 370, Issue 1, 15 March 2012, Pages 102-110, ISSN 0021-9797, <http://dx.doi.org/10.1016/j.jcis.2011.12.037>.

Concentration Model

APNModel_S1

Concentration model which is used by all other derived properties.

Takes $[S]_0$ and calculates the monomeric concentration $[S_1]$ as function of the *cmc* and the relative transition width *r*.

$$A = \frac{2}{1 + \sqrt{\frac{2}{\pi}} r e^{-\frac{1}{2r^2}} + \operatorname{erf}\left(\frac{1}{\sqrt{2}r}\right)}$$
$$[S_1] = cmc \left[1 - A \frac{1}{2} \left(\sqrt{\frac{2}{\pi}} r e^{-\frac{(s_0-1)^2}{2r^2}} + (s_0-1) \left(\operatorname{erf}\left(\frac{s_0-1}{\sqrt{2}r}\right) - 1 \right) \right) \right]$$

Function Name = APNModel_S1

Brief Description = APN Model: monomeric surfactant concentration - USC - Al-Soufi 2011

[Independent Variables]

cS0 =

[Dependent Variables]

cS1 =

[Fitting Parameters]

Names = cmc,r

Meanings = cmc,relative transition width

[Formula]

s0 = cS0/cmc;

A=2/(1+sqrt(2/Pi)*r*exp(-1/(2*r*r))+erf(1/Sqrt(2)/r));

cS1=cmc*(1 - (A/2)*(sqrt(2/Pi)*r*exp(-(s0-1)^2/(2*r*r)))+(s0-1)*(erf((s0-1)/(sqrt(2)*r))-1)));

Derived Properties

APNModel_DyeExchangeFluorFull

Fluorescence emission intensity of a dye in exchange equilibrium between the aqueous and the micellar pseudo-phase in a surfactant solution (Full version).

Takes $[S]_0$ and calculates the fluorescence intensity $F(\lambda, [S]_0)$ as function of the parameters cmc , the relative transition width r , the aggregation number n , the partition equilibrium constant K , and the limiting fluorescence intensities of free and bound dye (F_f , F_b).

$$F(\lambda, [S]_0) = F_f(\lambda) \cdot X_f + F_b(\lambda) \cdot X_b = \frac{F_f(\lambda) + F_b(\lambda) \cdot K \cdot [M]}{1 + K \cdot [M]}$$

This function needs the function APNModel_S1.

This same model can of course also be used for any other property of the form

$A([S]_0) = A_f \cdot X_f + A_b \cdot X_b$, such as the translational diffusion constant D .

The aggregation number n and the partition equilibrium constant K are fully correlated in this fit model ($K \cdot [M] = K \cdot [S_m] / n$) and can therefore not be determined simultaneously. The aggregation number n has to be treated as a constant and fixed during the fit. If n is unknown, then it should be fixed to $n=1$. In this case the fitted value of K is the ratio K/n .

The parameters cmc, K, F_f, F_b are actively initialized at the beginning of the fit, assuming that the data are sorted with respect to $[S]_0$ (ascending or descending).

Function Name = APNModel_DyeExchangeFluorFull

Brief Description = APN Model: Dye Exchange - USC - Al-Soufi 2013- V01

[Independent Variables]

cS0 =

[Dependent Variables]

F =

[Fitting Parameters]

Names = cmc, r, n, K, Ff, Fb

Meanings = cmc, relative transition width, aggregation number, K, F free dye, F bound dye

[Formula]

cS1 = nlf_APNModel_S1(cS0, cmc, r);

cSm = cS0 - cS1;

cM = cSm/n;

F = (Ff + Fb * K * cM) / (1 + K * cM);

APNModel_DyeExchangeFluorShort

Fluorescence emission intensity of a dye in exchange equilibrium between the aqueous and the micellar pseudo-phase in a surfactant solution (Short version).

This fit model is identical to APNModel_DyeExchangeFluorFull, except for the definition of the parameters. The limiting fluorescence intensities of free (F_f) and bound dye (F_b) are now expressed by the fluorescence intensity ratio $qbf = F_b/F_f$ and the limiting fluorescence intensities of free (F_f). Furthermore, in order to avoid the full correlation between the aggregation number n and the partition equilibrium constant K only the ratio $Kn = K/n$ is used as fit parameter.

The model takes $[S]_0$ and calculates the fluorescence intensity $F(\lambda, [S]_0)$ as function of the cmc , the relative transition width r , the ratio $Kn = K/n$ between the partition equilibrium constant K and the aggregation number n , the limiting fluorescence intensities of free (F_f , FA) and the fluorescence intensity ratio $qbf = F_b/F_f$.

$$F(\lambda, [S]_0) = F_f(\lambda) \cdot X_f + F_b(\lambda) \cdot X_b = \frac{F_f(\lambda) + qbf \cdot F_f(\lambda) \cdot Kn \cdot [S_m]}{1 + Kn \cdot [S_m]}$$

This function needs the function APNModel_S1.

This same model can of course also be used for any other property of the form $A([S]_0) = A_f \cdot X_f + A_b \cdot X_b$, such as the translational diffusion constant D .

The parameters cmc, Kn, Ff, qbf are actively initialized at the beginning of the fit, assuming that the data are sorted with respect to $[S]_0$ (ascending or descending).

```
Function Name = APNModel_DyeExchangeFluorShort
Brief Description = APN Model: Dye Exchange - USC - Al-Soufi 2013- V01
[Independent Variables]
cS0 =
[Dependent Variables]
F =
[Fitting Parameters]
Names = cmc,r,Kn,Ff,qbf
Meanings = cmc,relative transition width,K/n,Ffree,Fbound/Ffree
[Formula]
cS1= nlf_APNModel_S1(cS0,cmc,r);
cSm= cS0 - cS1;
Fb=Ff*qbf;
F= (Ff + Fb*Kn*cSm)/(1+Kn*cSm);
```

APNModel_AbsorptionBandRatio

Ratio of the direct absorption at two wavelengths λ_a and λ_b of a surfactant as function of the surfactant concentration.

Takes $[S]_0$ and calculates the ratio of the absorptions at two wavelengths λ_a and λ_b as function of the parameters cmc , the relative transition width r , and the molar absorptivity ratios q_1 , q_m , and q_a .

$$q(\lambda, [S]_0) = \frac{A(\lambda_b)}{A(\lambda_a)} = \frac{[S_1] \cdot q_1 + [S_m] \cdot q_m \cdot q_a}{[S_1] + [S_m] \cdot q_a}$$

with the molar absorptivity ratios:

$$q_1 = \frac{\varepsilon_1(\lambda_b)}{\varepsilon_1(\lambda_a)}, \quad q_m = \frac{\varepsilon_m(\lambda_b)}{\varepsilon_m(\lambda_a)}, \quad q_a = \frac{\varepsilon_m(\lambda_a)}{\varepsilon_1(\lambda_a)}$$

This function needs the function APNModel_S1.

The value of $q(\lambda, [S]_0=0) = q_1$ is treated separately.

```
Function Name = APNModel_AbsorptionBandRatio
Brief Description = APN Model: Absorption Band Ratio - USC - Al-Soufi 2013- V01
[Independent Variables]
cS0 =
[Dependent Variables]
q =
[Fitting Parameters]
Names = cmc,r,q1,qm,qa
Meanings = cmc,relative transition width,ratio momomers,ratio micellized,ratio
first band
[Formula]
cS1= nlf_APNModel_S1(cS0,cmc,r);
cSm= cS0 - cS1;
q= ( cS0>0 ? (cS1*q1+cSm*qm*qa)/(cS1 + cSm*qa) : q1);
```


APNModel_DyeExchangeFCS_tauDMean

Mean diffusion time $\bar{\tau}_D$ of a dye in fast exchange equilibrium between the aqueous and the micellar pseudo-phase in a surfactant solution.

The model takes $[S]_0$ and calculates the mean diffusion time $\bar{\tau}_D$ as function of the *cmc*, the relative transition width *r*, the ratio $Kn = K/n$, and the diffusion times of free ($\tau_{D,f}$) and bound dye ($\tau_{D,b}$):

$$\bar{\tau}_D = \frac{w_{xy}^2}{4D} = \frac{\tau_{D,f}(1+K\cdot[M])}{1 + \frac{\tau_{D,f}}{\tau_{D,b}}K\cdot[M]} = \frac{\tau_{D,f}(1+Kn\cdot[S_m])}{1 + \frac{\tau_{D,f}}{\tau_{D,b}}Kn\cdot[S_m]}$$

In order to avoid the full correlation between the aggregation number *n* and the partition equilibrium constant *K* only the ratio $Kn = K/n$ is used as fit parameter.

This function needs the function APNModel_S1.

```
Function Name = APNModel_DyeExchangeFCS_tauDMean
Brief Description = APN Model: Dye Exchange - USC - Al-Soufi 2013- V01
[Independent Variables]
cS0 =
[Dependent Variables]
tD =
[Fitting Parameters]
Names = cmc,r,Kn,tDf,tDb
Meanings = cmc,relative transition width,K/n,tauD free dye,tauD bound dye
[Formula]
cS1= nlf_APNModel_S1(cS0,cmc,r);
cSm= cS0 - cS1;
tD = tDf*(1+Kn*cSm)/(1 + (tDf/tDb) * Kn*cSm);
```

Other models used before:

APNModel_Conductivity

Conductivity of a surfactant solution.

Takes $[S]_0$ and calculates the conductivity κ as function of the *cmc*, the relative transition width *r* and the slopes *a* and *b*, and the solvent conductivity $c = \kappa_s$.

$$\kappa = a[S_1] + b[S_m]/n + c = a[S_1] + b[S_m] + c$$

This function needs the function APNModel_S1.

The parameters *cmc*, *a*, *b*, *c* are actively initialized at the beginning of the fit, assuming that the data are sorted with respect to $[S]_0$ (ascending or descending).

```
Function Name = APNModel_Conductivity
Brief Description = APN Model: Electric conductivity - USC - Al-Soufi 2011
[Independent Variables]
cS0 =
[Dependent Variables]
k =
[Fitting Parameters]
Names = cmc,r,a,b,c
Meanings = cmc,relative transition width,a,b,c
[Formula]
cS1= nlf_APNModel_S1(cS0,cmc,r);
cSm= cS0 - cS1;
k=a* cS1 +b * cSm + c;
```

APNModel_Conductivity_k1

Conductivity of a surfactant solution. Limiting Straight Line 1, below the *cmc*.

Utility Function: Takes $[S]_0$ and calculates the limiting straight line κ_1 , below the *cmc* of the plot of the conductivity κ vs. $[S]_0$ with the parameters *cmc*, *r*, *a*, *b*, *c* determined with APNModel_Conductivity.

$$\kappa_1 = a[S]_0 + c$$

The parameters *cmc*, *r* *y* *b* are not needed, but included for consistency.

Function Name = APNModel_Conductivity_k1
Brief Description = APN Model: Electric conductivity Line 1- USC - Al-Soufi 2011
[Independent Variables]
cS0 =
[Dependent Variables]
k1 =
[Fitting Parameters]
Names = *cmc*,*r*,*a*,*b*,*c*
Meanings = *cmc*,relative curvature,*a*,*b*,*c*
[Formula]
k1 = a* cS0 + c;

APNModel_Conductivity_k2

Conductivity of a surfactant solution. Limiting Straight Line 1, below the *cmc*.

Utility Function: Takes $[S]_0$ and calculates the limiting straight line κ_2 , above the *cmc* of the plot of the conductivity κ vs. $[S]_0$ with the parameters *cmc*, *r*, *a*, *b*, *c* determined with APNModel_Conductivity.

$$\kappa_2 = a \cdot cmc + b \cdot ([S]_0 - cmc) + c$$

The parameter *r* is not needed, but included for consistency.

Function Name = APNModel_Conductivity_k2
Brief Description = APN Model: Electric conductivity Line 2- USC - Al-Soufi 2011
[Independent Variables]
cS0 =
[Dependent Variables]
k2 =
[Fitting Parameters]
Names = *cmc*,*r*,*a*,*b*,*c*
Meanings = *cmc*,relative curvature,*a*,*b*,*c*
[Formula]
k2=a* cmc b*(cS0-cmc)+ c;

APNModel_MolarConductivity

Molar conductivity of a surfactant solution.

Takes $[S]_0$ and calculates the molar conductivity (equivalent conductance) as function of the *cmc*, the relative transition width *r* and the slopes *a* and *b*.

$$\Lambda_m = a[S_1]/[S]_0 + b[S_m]/[S]_0$$

This function needs the function APNModel_S1.

Function Name = APNModel_MolarConductivity
Brief Description = APN Model: Electric molar conductivity - USC - Al-Soufi 2011
[Independent Variables]
cS0 =
[Dependent Variables]
k =
[Fitting Parameters]
Names = *cmc*,*r*,*a*,*b*
Meanings = *cmc*,relative transition width,*a*,*b*
[Formula]

```
cS1= nlf_APNModel_S1(cS0,cmc,r);  
cSm= cS0 - cS1;  
k=a* cS1/cS0 +b * cSm/cS0;
```

APNModel_SelfDiffusion

Self-diffusion coefficient of a surfactant solution.

Takes $[S]_0$ and calculates the self-diffusion coefficient D_{obs} as function of the cmc , the relative transition width r and the self-diffusion coefficients of monomeric (D_1) and micellized (D_m) surfactants.

$$D_{obs} = D_1 \cdot \frac{[S_1]}{[S]_0} + D_m \cdot \frac{[S_m]}{[S]_0}$$

This function needs the function APNModel_S1.

```
Function Name = APNModel_SelfDiffusion  
Brief Description = APN Model: Self Diffusion Coefficients - USC - Al-Soufi 2011  
[Independent Variables]  
cS0 =  
[Dependent Variables]  
Dobs =  
[Fitting Parameters]  
Names = cmc,r,D1,Dm  
Meanings = cmc,relative transition width,D1,Dm  
[Formula]  
cS1= nlf_APNModel_S1(cS0,cmc,r);  
cSm= cS0 - cS1;  
Dobs = (D1* cS1+Dm *cSm)/cS0;
```

APNModel_NMRChemicalShifts

NMR Chemical Shifts of a surfactant solution.

Takes $[S]_0$ and calculates the NMR Chemical Shifts as function of the cmc , the relative transition width r and the chemical shifts of monomeric (d_1) and micellized (d_m) surfactants.

$$\delta_{obs} = \delta_1 \cdot \frac{[S_1]}{[S]_0} + \delta_m \cdot \frac{[S_m]}{[S]_0}$$

This function needs the function APNModel_S1.

```
Function Name = APNModel_NMRChemicalShifts  
Brief Description = APN Model: NMR Chemical Shifts - USC - Al-Soufi 2011  
[Independent Variables]  
cS0 =  
[Dependent Variables]  
Dobs =  
[Fitting Parameters]  
Names = cmc,r,d1,dm  
Meanings = cmc,relative transition width,d1,dm  
[Formula]  
cS1= nlf_APNModel_S1(cS0,cmc,r);  
cSm= cS0 - cS1;  
dobs = (d1* cS1+dm *cSm)/(cS1+cSm);
```

APNModel_SurfaceTensionSzyszkowski

Surface Tension (Szyszkowski Equation) of a surfactant solution.

Takes $[S]_0$ and calculates the Surface Tension γ (g) using the Szyszkowski Equation as function of the *cmc*, the relative transition width *r*, the adsorption equilibrium constant K_{ad} , the surface tension of the solvent γ_0 (*g0*), and the constant $a = RT/\omega$, being ω the cross sectional area of the surfactant molecule at the surface per mol.

$$\gamma = \gamma_0 - a \ln(1 + K_{ad} \cdot [S_1])$$

This function needs the function APNModel_S1.

Function Name = APNModel_SurfaceTensionSzyszkowski

Brief Description = APN Model: Surface Tension (Szyszkowski Equation) - USC - Al-Soufi 2011

[Independent Variables]

cS0 =

[Dependent Variables]

g =

[Fitting Parameters]

Names = cmc,r,a,Kad,g0

Meanings = cmc,relative transition width,(R T)/omega,adsorption equilibrium constant,g0

[Formula]

cS1= nlf_APNModel_S1(cS0,cmc,r);

g=g0 - a* ln(1+ Kad*cS1);

Utility functions

APNModel_d2S1

First derivative of the monomeric surfactant concentration (equation (10)).

Takes $[S]_0$ and calculates the first derivative $[S_1]'$ (gradient) of the monomeric concentration $[S_1]$ as function of the *cmc* and the relative transition width r .

$$A = \frac{2}{1 + \sqrt{\frac{2}{\pi}} r e^{-\frac{1}{2r^2}} + \operatorname{erf}\left(\frac{1}{\sqrt{2}r}\right)} \quad [S_1]' = \frac{d[S_1]}{d[S]_0} = \frac{A}{2} \left(1 - \operatorname{erf}\left(\frac{s_0 - 1}{\sqrt{2}r}\right) \right)$$

Function Name = APNModel_d2S1

Brief Description = APN Model: first derivative of monomeric surfactant concentration - USC - Al-Soufi 2011

[Independent Variables]

cS0 =

[Dependent Variables]

d1S1 =

[Fitting Parameters]

Names = cmc,r

Meanings = cmc,relative transition width

[Formula]

s0 = cS0/cmc;

A=2/(1+sqrt(2/Pi)*r*exp(-1/(2*r*r))+erf(1/Sqrt(2)/r));

d1S1=(A/2)*(1-erf((s0-1)/(sqrt(2)*r)));

APNModel_d2S1

Second derivative of the monomeric surfactant concentration (equation (7)).

Takes $[S]_0$ and calculates the second derivative $[S_1]''$ (curvature) of the monomeric concentration $[S_1]$ as function of the *cmc* and the relative transition width r .

$$A = \frac{2}{1 + \sqrt{\frac{2}{\pi}} r e^{-\frac{1}{2r^2}} + \operatorname{erf}\left(\frac{1}{\sqrt{2}r}\right)} \quad [S_1]'' = \frac{d^2[S_1]}{ds_0^2} = -\frac{A}{cmc} \frac{1}{\sqrt{2\pi}r} e^{-\frac{(s_0-1)^2}{2r^2}}$$

Function Name = APNModel_d2S1

Brief Description = APN Model: second derivative of monomeric surfactant concentration - USC - Al-Soufi 2011

[Independent Variables]

cS0 =

[Dependent Variables]

d2S1 =

[Fitting Parameters]

Names = cmc,r

Meanings = cmc,relative transition width

[Formula]

s0 = cS0/cmc;

A=2/(1+sqrt(2/Pi)*r*exp(-1/(2*r*r))+erf(1/Sqrt(2)/r));

d2S1=-(A/(cmc*sqrt(2*Pi)*r))*exp(-(s0-1)^2/(2*r*r));