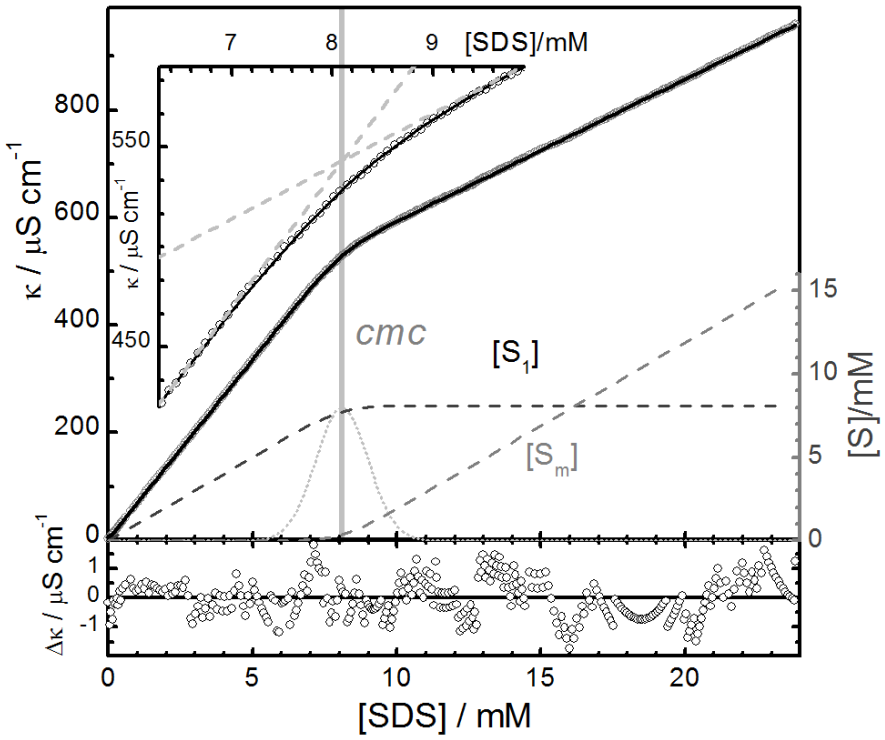

APNModel Fitting-Functions for the APN-Model Origin Data Analysis Software

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www.usc.es/fotofqm/en/units/single-molecule-fluorescence/concentration-model-surfactants-near-cmc

Contents

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References

Please cite the following articles:

- 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**, 370, 2012, 102-110, DOI: 10.1016/j.jcis.2011.12.037.
- Lucas Piñeiro, Sonia Freire, Jorge Bordello, Mercedes Novo, and Wajih Al-Soufi, *Dye Exchange in Micellar Solutions. Quantitative Analysis of Bulk and Single Molecule Fluorescence Titrations.* **Soft Matter,** 2013,9, 10779-10790**,** DOI: 10.1039/c3sm52092g
- Lucas Piñeiro, Mercedes Novo, and Wajih Al-Soufi, *Fluorescence Emission of Pyrene in Surfactant Solutions.,* **Advances in Colloid and Interface Science,** 2015, 215, 1–12. DOI:10.1016/j.cis.2014.10.010

Change History

V2.1c 2017

- add more detailed instructions for the installation of the APN-functions

V2.1 2014

- include new functions published in Piñeiro 2015

V2.0 2013-12-18

- all functions changed to Origin C in order to avoid conflicts of parameter names with Origin
- include new functions published in Piñeiro 2013

V1.0 2012-01-12 Published Version in Al-Soufi 2012

How to use in Origin Data Analysis Software

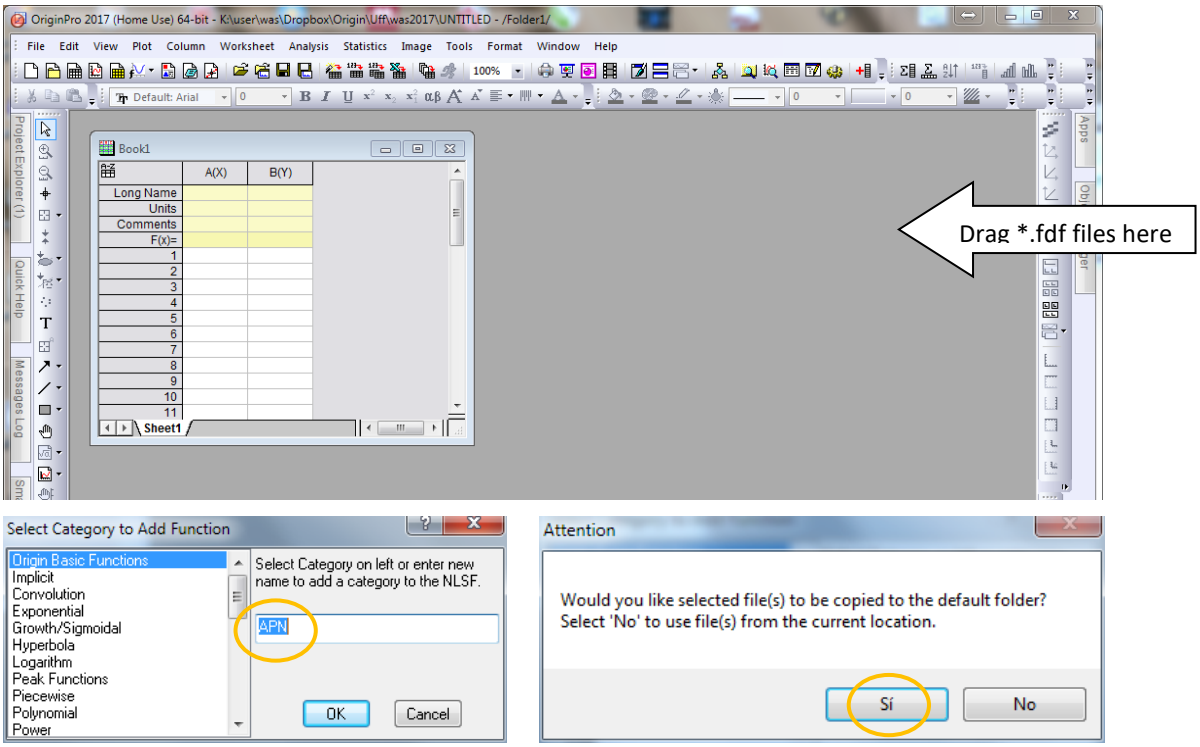
We provide the "APN-model" as fitting functions for the Origin Data Analysis Software (OriginLab Corporation, Northampton, MA 01060, USA) in a compressed zip-archive. Updated versions can be downloaded from the author's webpage.

The functions were tested with Origin 8.5 SR1, Origin 9.1, Origin 2018

Add the fitting functions to Origin

The functions of the APN-model have to be added to Origin:

1. Decompress the zip-archive with the APN-Functions in a temporal directory
2. Drag the functions (*.fdf) to the open Origin Workspace (grey area in Origin).
   Create a new category "APN".
   Allow to copy them to the default folder.



(Alternatively use the **fitting function organizer**. *Do not* copy directly to the user directory.)

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)`".

Update existing functions

In order to *update existing functions,* copy the new version to the Origin user directory "Origin\UFF*user*\fitfunc". Don't add *new* functions in this way!

Example: cmc of SDS from Electrical Conductivity Data

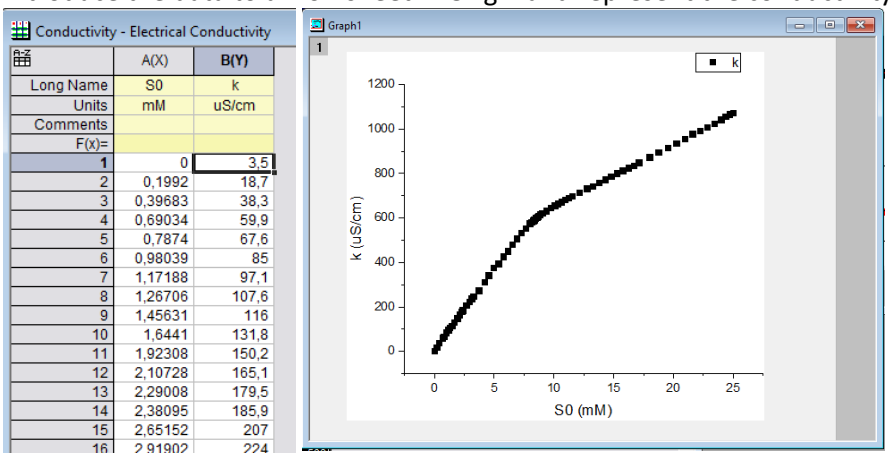
The **conductivity of a solution of ionic surfactants** of concentration $[S]_0$ is given by

$$\kappa = a[S_1] + b[S_m] + c \qquad (1.1)$$

We measured the electrical conductivity of the **anionic surfactant SDS** in water at 25ºC as a function of the concentration of SDS, $[S]_0$ = [SDS].

In order to determine the *cmc* we use Origin in order to perform a **nonlinear curve fit** of the model function "APNModel_Conductivity" to the data.

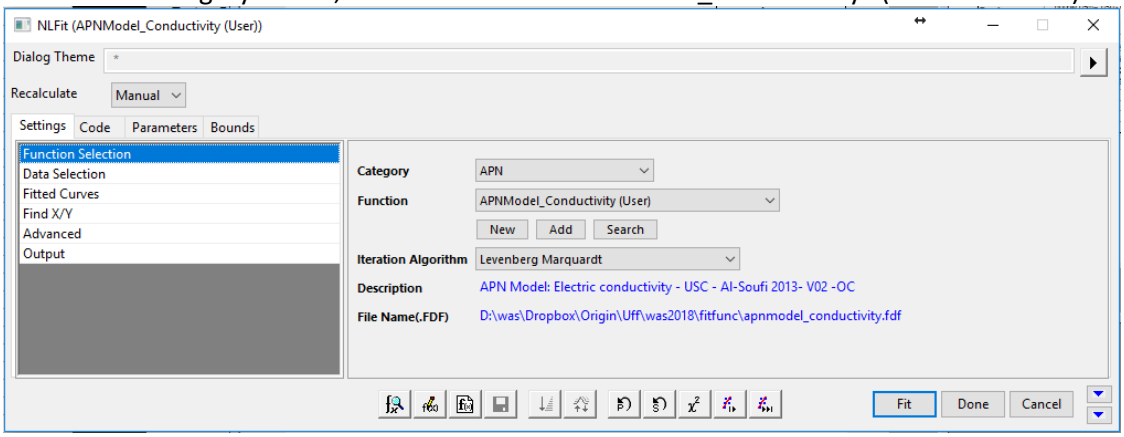
1) Introduce the data to a worksheet in Origin and represent the conductivity



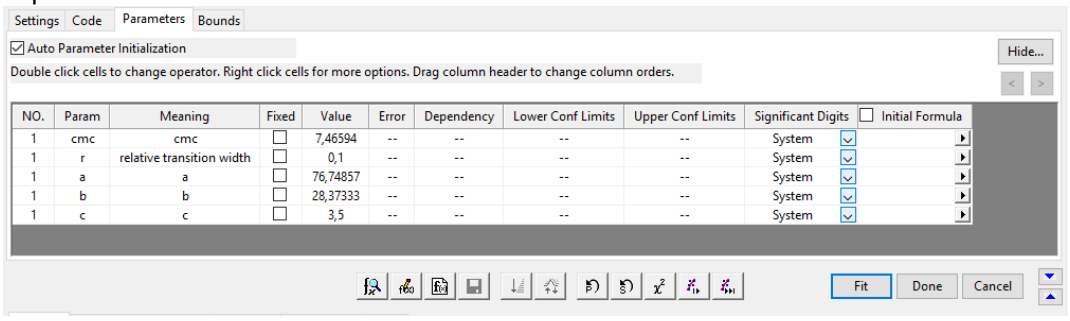
Conductivity - Electrical Conductivity

	A(X)	B(Y)
Long Name	S0	k
Units	mM	uS/cm
Comments		
F(x)=		
1	0	3,5
2	0,1992	18,7
3	0,39683	38,3
4	0,69034	59,9
5	0,7874	67,6
6	0,98039	85
7	1,17188	97,1
8	1,26706	107,6
9	1,45631	116
10	1,6441	131,8
11	1,92308	150,2
12	2,10728	165,1
13	2,29008	179,5
14	2,38095	185,9
15	2,65152	207
16	2,91902	224

2) Open the **nonlinear curve fit** dialog (Analysis > Fitting > Nonlinear Curve Fit > Open Dialog) or type Ctrl-Y with the Graph window active.
Choose the Category "APN", and the Function "APNModel_Conductivity" (See installation)



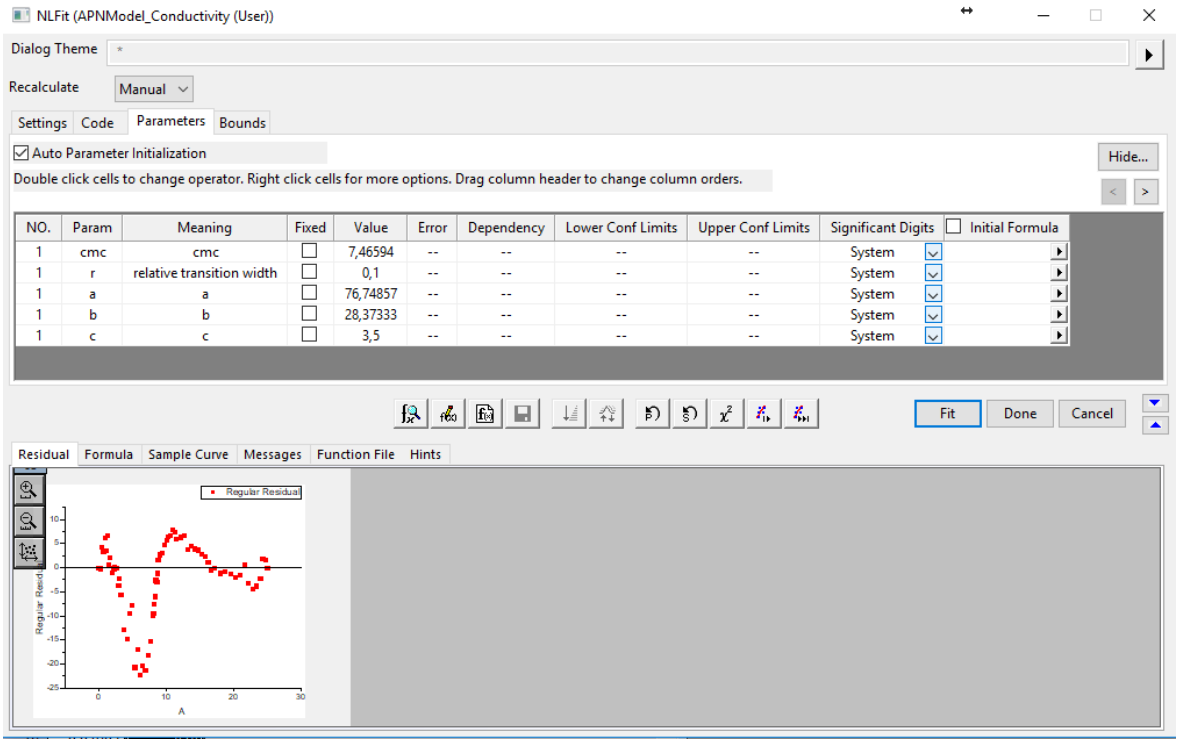
3) Change to the "Parameters" tab and adjust the initial parameters. The auto parameter initialization will have chosen some initial values for the parameters. Check their values in the Graph window. The calculated curve should be already a good representation of your experimental data.



NO.	Param	Meaning	Fixed	Value	Error	Dependency	Lower Conf Limits	Upper Conf Limits	Significant Digits	Initial Formula
1	cmc	cmc	☐	7,46594	--	--	--	--	System	
1	r	relative transition width	☐	0,1	--	--	--	--	System	
1	a	a	☐	76,74857	--	--	--	--	System	
1	b	b	☐	28,37333	--	--	--	--	System	
1	c	c	☐	3,5	--	--	--	--	System	

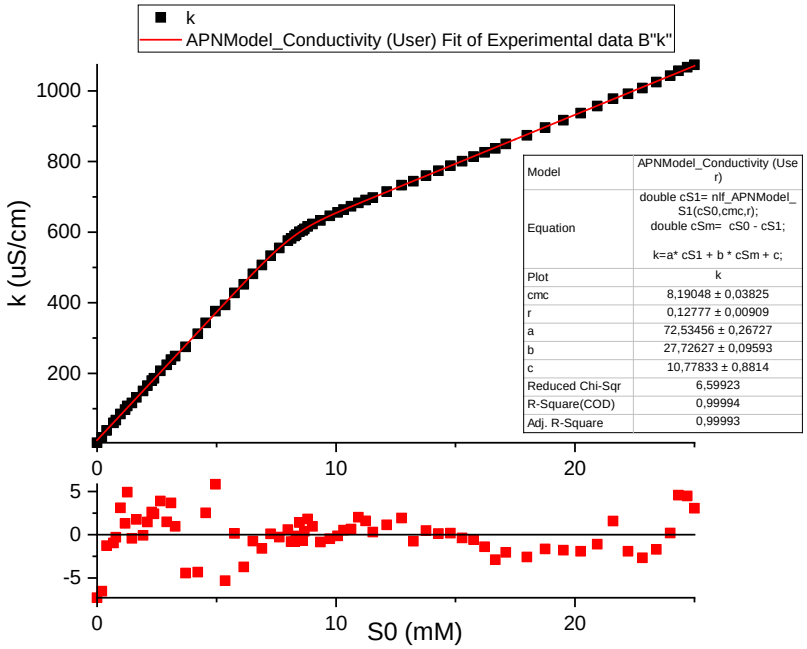
4) Depending on the data quality you may first fix some of the parameters, for example the value of *r* or the *cmc* itself. Click on the "Fit until converged" button  . Observe the fit in the Graph window. Once the slopes *a* and *b* and the residual conductivity *c* is fitted, repeat the fit with all the parameters free.

Initial Values:



Once the fit has converged, click on "OK" or "Done" and go back to the Graph window.

5) The fit yields a value of *cmc* = 8.190 ± 0.038 mM with *r* = 0.127 ± 0.009.
Observe that in this case the residuals are much lower than 1% of the conductivity value, even within the *cmc* region.



Fitting functions for Origin Data Analysis Software

In the following sections we describe in detail the fitting functions supplied for Origin.

Concentration Model

APNModel_S1

Concentration model, 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*.

$$A = \frac{2}{1+\sqrt{\frac{2}{\pi}}\, r\, \mathrm{e}^{-\frac{1}{2r^2}} + \mathrm{erf}\left(\frac{1}{\sqrt{2}\, r}\right)}$$

$$[\mathrm{S}_1] = cmc\left[1 - A\frac{1}{2}\left(\sqrt{\frac{2}{\pi}}\, r\, \mathrm{e}^{-\frac{(s_0-1)^2}{2r^2}} + (s_0-1)\left(\mathrm{erf}\left(\frac{s_0-1}{\sqrt{2}r}\right)-1\right)\right)\right]$$

```
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)
));
```

Direct Surfactant Properties:

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 $c = \kappa_s$.

$$\kappa = a[\mathrm{S}_1] + b'[\mathrm{S}_m]/n + c = a[\mathrm{S}_1] + b[\mathrm{S}_m] + c$$

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 $a = R{\cdot}T/\omega$, 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 equlibrium constant,g0
[Formula]
cS1= nlf_APNModel_S1(cS0,cmc,r);
g=g0 - a* ln(1+ Kad*cS1);
```

Dye Exchange

For more details, see Piñeiro 2013.

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 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, Ff,Fb` 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:

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

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 $\overline{\tau}_D$ 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 $\overline{\tau}_D$ 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 $(\tau_{D,b})$:

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

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);
```

Pyrene Fluorescence

For more details, see Piñeiro 2015.

APNModel_PyreneFluorIntensity

Fluorescence emission intensity of a dye (pyrene) in exchange equilibrium between the aqueous and the micellar pseudo-phase in a surfactant solution.
Takes $[S]_0$ and calculates the fluorescence intensity $I^{(\lambda)}([S]_0)$ as function of the following parameters:

$$I^{(\lambda)}([S]_0) = I_{f,nq}^{(\lambda)} + I_{bm}^{(\lambda)} + I_{be}^{(\lambda)} = I_f^{(\lambda)}\left(X_f X_{nq} + q_{bm,f}^{(\lambda)} X_b X_{bm} + q_{be,f}^{(\lambda)} X_b X_{be}\right)$$

$$q_{bm,f}^{(\lambda)} = \frac{F_{bm}^{(\lambda)}}{F_f^{(\lambda)}},\ q_{be,f}^{(\lambda)} = \frac{F_{be}^{(\lambda)}}{F_f^{(\lambda)}}$$

with

$$X_f = \frac{1}{1+K\cdot[M]},\ X_b = 1 - X_f,\ X_{nq} = \frac{1}{1+K_q[S_1]},\ \overline{i} = \frac{[D_b]}{[M]} = [D]_0\cdot K\cdot X_f$$

$$X_{bm} = e^{-\overline{i}}\sum_{i=0}^{\infty}\frac{1}{1+iK'_{be}}\frac{\overline{i}^{\,i}}{i!},\qquad X_{be} = 1 - X_{bm}$$

$[S_1]$ and $[S_m]$ are calculated with the surfactant concentration model (APNModel).
$[D]_0$ is necessary for the determination of the mean occupancy.

Parameter	Variable	
cmc	cmc	critical micelle concentration
r	r	relative transition width
n	n	aggregation number
K	K	binding equilibrium constant
cD0	$[D]_0$	total dye concentration

Kq	K_q	quenching equilibrium constant
KeV	$K'_{be} = K_{be} / V_m$	excimer formation constant
IfL	$I_f^{(\lambda)} = F_f^{(\lambda)}[D]_0$	fluorescence intensity of free dye at wavelength λ
qbmfL	$q_{bm,f}^{(\lambda)} = F_{bm}^{(\lambda)} / F_f^{(\lambda)}$	fluorescence intensity ratio of **bound monomer** and **free** dye at wavelength λ
qbefL	$q_{be,f}^{(\lambda)} = F_{be}^{(\lambda)} / F_f^{(\lambda)}$	fluorescence intensity ratio of **bound excimer** and **free** dye at wavelength λ

```
[Fitting Parameters]
Names = cmc,r,n,K,cD0,Kq,KeV,IfL,qbmfL,qbefL

[Independent Variables]
cS0 =

[Dependent Variables]
IL =

[Formula]
double cS1, cSm, cM, Xf, Xb, im, Xnq, Xbm, Xbe, imMin,ifac;
int ii;

// call concentration model APNModel
cS1= nlf_APNModel_S1(cS0,cmc,r);
cSm= cS0 - cS1;
cM=cSm/n;

// fractions
Xf= 1/(1+K*cM);
Xb= 1-Xf;
Xnq = 1/(1+Kq*cS1);

// mean occupancy im
im = cD0*K*Xf;

// determine Xbm and Xbe iteratively
// number of terms to be summed up
imMin = ceil(6+3*im);
// initialize
Xbm=1; // term with i=0
ifac=1;
for(ii = 1; ii < imMin; ii++) // start with i=1 (term with i=0 is 1)
{
       //increase factorial ifac=i!
       ifac*=ii;
       // add next summand
       Xbm += pow(im,ii)/(ifac*(1+ii*KeV));
}
Xbm *=exp(-im);
Xbe = 1 - Xbm;

IL= IfL*(Xf*Xnq + qbmfL*Xb*Xbm + qbefL*Xb*Xbe);
```

APNModel_PyreneFluorSRMonExc

Spectral Ratio at two wavelength of the fluorescence emission intensity of a dye (pyrene) in exchange equilibrium between the aqueous and the micellar pseudo-phase in a surfactant solution.

Takes $[S]_0$ and calculates the spectral ratio of the fluorescence intensities $I^{(\lambda)}([S]_0)$ as function of the following parameters:

$$SR^{(2,1)} = \frac{I^{(2)}}{I^{(1)}} \approx \frac{SR_f^{(2,1)} X_f X_{nq} + SR_{bm}^{(2,1)} q_{bm,f}^{(1)} X_b X_{bm} + q_{be,f}^{(2,1)} X_b X_{be}}{X_f X_{nq} + q_{bm,f}^{(1)} X_b X_{bm}}$$

This general function can be used for the monomer-monomer ratio $SR_m^{(2,1)} = I^{(2)} / I^{(1)}$

$$SR_m^{(2,1)} = \frac{I^{(2)}}{I^{(1)}} \approx \frac{SR_f^{(2,1)} X_f X_{nq} + SR_{bm}^{(2,1)} q_{bm,f}^{(1)} X_b X_{bm}}{X_f X_{nq} + q_{bm,f}^{(1)} X_b X_{bm}} \text{ with } q_{be,f}^{(2,1)} = 0$$

and also for the excimer-monomer ratio $SR_e^{(e,1)} = I^{(e)} / I^{(1)}$

$$SR_e^{(e,1)} = \frac{I^{(e)}}{I^{(1)}} \approx \frac{SR_f^{(e,1)} X_f X_{nq} + SR_{bm}^{(e,1)} q_{bm,f}^{(1)} X_b X_{bm} + q_{be,f}^{(e,1)} X_b X_{be}}{X_f X_{nq} + q_{bm,f}^{(1)} X_b X_{bm}}$$

$$SR_f^{(2,1)} = \frac{F_f^{(2)}}{F_f^{(1)}},\ SR_f^{(e,1)} = \frac{F_f^{(e)}}{F_f^{(1)}},\ SR_{bm}^{(2,1)} = \frac{F_{bm}^{(2)}}{F_{bm}^{(1)}},\ SR_{bm}^{(e,1)} = \frac{F_{bm}^{(e)}}{F_{bm}^{(1)}}$$

$$q_{bm,f}^{(1)} = \frac{F_{bm}^{(1)}}{F_f^{(1)}},\ q_{be,f}^{(e,1)} = \frac{F_{be}^{(e)}}{F_f^{(1)}}$$

with

$$X_f = \frac{1}{1 + K \cdot [\mathrm{M}]},\ X_b = 1 - X_f,\ X_{nq} = \frac{1}{1 + K_q [\mathrm{S}_1]},\ \bar{i} = \frac{[\mathrm{D_b}]}{[\mathrm{M}]} = [\mathrm{D}]_0 \cdot K \cdot X_f,\ X_{bm} = e^{-\bar{i}} \sum_{i=0}^{\infty} \frac{1}{1 + iK'_{be}} \frac{\bar{i}^{\,i}}{i!},\quad X_{be} = 1 - X_{bm}$$

$[S_1]$ and $[S_m]$ are calculated with the surfactant concentration model (APNModel).
$[D]_0$ is necessary for the determination of the mean occupancy.

Parameter	Variable	
cmc	cmc	critical micelle concentration
r	r	relative transition width
n	n	aggregation number
K	K	binding equilibrium constant
cD0	$[D]_0$	total dye concentration
Kq	K_q	quenching equilibrium constant
KeV	$K'_{be} = K_{be} / V_m$	excimer formation constant
SRf21	$SR_f^{(2,1)} = F_f^{(2)} / F_f^{(1)}$	fluorescence intensity ratio of **free** dye at λ_2 and λ_1
SRbm21	$SR_{bm}^{(2,1)} = F_{bm}^{(2)} / F_{bm}^{(1)}$	fluorescence intensity ratio of **bound monomer** at λ_2 and λ_1
qbef21	$q_{be,f}^{(2,1)} = F_{be}^{(2)} / F_f^{(1)}$	fluorescence intensity ratio of **bound excimer** and **free** dye at λ_2 and λ_1
qbmf1	$q_{bm,f}^{(1)} = F_{bm}^{(1)} / F_f^{(1}$	fluorescence intensity ratio of **bound monomer** and **free** dye at λ_1

```
[Fitting Parameters]
Names = cmc,r,n,K,cD0,Kq,KeV,SRf21,SRbm21,qbef21,qbmf1

[Independent Variables]
cS0 =

[Dependent Variables]
SR21 =

[Formula]
double cS1, cSm, cM, Xf, Xb, im, Xnq, Xbm, Xbe, imMin;
int ii, ifac;

// call concentration model APNModel
cS1= nlf_APNModel_S1(cS0,cmc,r);
cSm= cS0 - cS1;
cM=cSm/n;

// fractions
Xf= 1/(1+K*cM);
Xb= 1-Xf;
Xnq = 1/(1+Kq*cS1);
```

```
// mean occupancy im
im = cD0*K*Xf;

// determine Xbm and Xbe iteratively
// number of terms to be summed up
imMin = ceil(6+3*im);
// initialize
Xbm=1; // term with i=0
ifac=1;
for(ii = 1; ii < imMin; ii++) // start with i=1 (term with i=0 is 1)
{
 //increase factorial ifac=i!
 ifac*=ii;
 // add next summand
 Xbm += pow(im,ii)/(ifac*(1+ii*KeV));
}
Xbm *=exp(-im);
Xbe = 1 - Xbm;

SR21= (SRf21*Xf*Xnq + SRbm21*qbmf1*Xb*Xbm + qbef21*Xb*Xbe) / (Xf*Xnq + qbmf1*Xb*Xbm);
```

APNModel_PyreneFluorDecayMon

Time resolved intensity in the monomer band of the fluorescence emission of a dye (pyrene) in exchange equilibrium between the aqueous and the micellar pseudo-phase in a surfactant solution.
Takes $[S]_0$ and calculates the spectral ratio of the fluorescence intensities $I^{(\lambda)}([S]_0)$ as function of the following parameters:

$$I(t) = A_s\, e^{-t/\tau_s} + A_f I_f(t) + A_{bm} I_{bm}(t)$$

$$I_f(t) = F_f X_f X_{nq} [D]_0\, e^{-k_f t}$$

$$I_{bm}(t) = F_{bm} X_b [D]_0\, e^{\bar{i}\left(e^{-k'_1 t}-1\right)-k_m t} = F_{bm} X_b [D]_0\, e^{\bar{i}\left(e^{-K'_{be} k_m t}-1\right)-k_m t}$$

with

$$k'_{be} = \frac{k_1}{V_m}\ K'_{be} = \frac{k_1}{k_m}\frac{1}{V_m}$$

$$X_f = \frac{1}{1+K\cdot[M]},\ X_b = 1 - X_f,\ X_{nq} = \frac{1}{1+K_q[S_1]},\ \bar{i} = \frac{[D_b]}{[M]} = [D]_0 \cdot K \cdot X_f$$

$[S_1]$ and $[S_m]$ are calculated with the surfactant concentration model (APNModel).
$[D]_0$ is necessary for the determination of the mean occupancy.
Fractions X_f, X_{nq}, X_b are applied for correct amplitudes in global fits (X_{bm} is not taken into account).

Parameter	Variable	
cmc	cmc	critical micelle concentration
r	r	relative transition width
n	n	aggregation number
K	K	binding equilibrium constant
cD0	$[D]_0$	total dye concentration
Kq	K_q	quenching equilibrium constant
KeV	$K'_{be} = K_{be} / V_m$	excimer formation constant $K'_{be} = k_1/(k_m V_m)$
km	k_m	bound monomer decay rate constant
I0	I_0	residual fluorescence intensity (baseline)
t0	t_0	time shift
ts	τ_s	lifetime of surfactant or impurities (component with short lifetime)

tf	τ_f	lifetime of free dye
As	A_s	amplitude of surfactant or impurities
Af	A_f	amplitude of free dye
Abm	A_{bm}	amplitude of bound monomer
cS0	$[S]_0$	total surfactant concentration

```
[Fitting Parameters]
Names = cmc,r,n,K,cD0,Kq,KeV,km,I0,t0,ts,tf,As,Af,Abm,cS0

[Independent Variables]
t =

[Dependent Variables]
I =

[Formula]
// call concentration model APNModel
double cS1= nlf_APNModel_S1(cS0,cmc,r);
double cSm= cS0 - cS1;
double cM=cSm/n;

// fractions
double Xf= 1/(1+K*cM);
double Xb= 1-Xf;
double Xnq = 1/(1+Kq*cS1);

// mean occupancy im
double im = cD0*K*Xf;

// this is a tail-fit, so shift t=0 to the pulse position
double tt = t-t0;

double If  = Xf*Xnq * exp(-tt/tf);
double Ibm = Xb* exp(im*exp(-KeV*km*tt)-im - km*tt);

I = I0 + As*exp(-tt/ts) + Af*If + Abm*Ibm;
```

APNModel_PyreneFluorDecayMonExc

Time resolved intensity in the monomer band of the fluorescence emission of a dye (pyrene) in exchange equilibrium between the aqueous and the micellar pseudo-phase in a surfactant solution.

Takes $[S]_0$ and calculates the spectral ratio of the fluorescence intensities $I^{(\lambda)}([S]_0)$ as function of the following parameters:

$$I(t) = A_s\, e^{-t/\tau_s} + A_f I_f(t) + A_{bm} I_{bm}(t) + A_{be} I_{be}(t)$$

$$I_f(t) = F_f X_f X_{nq} [D]_0\, e^{-k_f t}$$

$$I_{bm}(t) = F_{bm} X_b [D]_0\, e^{\bar{i}\left(e^{-k'_1 t}-1\right)-k_m t} = F_{bm} X_b [D]_0\, e^{\bar{i}\left(e^{-K'_{be} k_m t}-1\right)-k_m t}$$

$$I_{be}(t) = F_{be} X_b [D]_0\, e^{-\bar{i}} \sum_{i=0}^{\infty} \frac{\bar{i}^{\,i}}{i!} \frac{K'_{be} i}{1 + K'_{be} i - k_e / k_m} \left(e^{-k_e t} - e^{-k_m (1 + K'_{be} i) t} \right)$$

with

$$k'_{be} = \frac{k_1}{V_m} \quad K'_{be} = \frac{k_1}{k_m} \frac{1}{V_m}$$

$$X_f = \frac{1}{1 + K \cdot [M]}, \quad X_b = 1 - X_f, \quad X_{nq} = \frac{1}{1 + K_q [S_1]}, \quad \bar{i} = \frac{[D_b]}{[M]} = [D]_0 \cdot K \cdot X_f$$

$[S_1]$ and $[S_m]$ are calculated with the surfactant concentration model (APNModel).

$[D]_0$ is necessary for the determination of the mean occupancy.
Fractions X_f, X_{nq}, X_b are applied for correct amplitudes in global fits (X_{bm} and X_{be} are not taken into account).

Parameter	Variable	
cmc	cmc	critical micelle concentration
r	r	relative transition width
n	n	aggregation number
K	K	binding equilibrium constant
cD0	$[D]_0$	total dye concentration
Kq	K_q	quenching equilibrium constant
KeV	$K'_{be} = K_{be} / V_m$	excimer formation constant $K'_{be} = k_1 / (k_m V_m)$
km	$k_m=(\tau_m)^{-1}$	bound monomer decay rate constant
ke	$k_e=(\tau_e)^{-1}$	bound excimer decay rate constant
I0	I_0	residual fluorescence intensity (baseline)
t0	t_0	time shift
ts	τ_s	lifetime of surfactant or impurities (component with short lifetime)
tf	τ_f	lifetime of free dye
As	A_s	amplitude of surfactant or impurities
Af	A_f	amplitude of free dye
Abm	A_{bm}	amplitude of bound monomer
Abe	A_{be}	amplitude of bound excimer
cS0	$[S]_0$	total surfactant concentration

```
[Fitting Parameters]
Names = cmc,r,n,K,cD0,Kq,KeV,km,ke,I0,t0,ts,tf,As,Af,Abm,Abe,cS0

[Independent Variables]
t =

[Dependent Variables]
It =

[Formula]
// call concentration model APNModel
double cS1= nlf_APNModel_S1(cS0,cmc,r);
double cSm= cS0 - cS1;
double cM= cSm/n;

// fractions
double Xf= 1/(1+K*cM);
double Xb= 1-Xf;
double Xnq = 1/(1+Kq*cS1);

// mean occupancy im
double im = cD0*K*Xf;

// this is a tail-fit, so shift t=0 to the pulse position
double tt = t-t0;

// Free dye
double If  = Xf*Xnq * exp(-tt/tf);

// Bound Monomer
double Ibm = Xb* exp(im*exp(-KeV*km*tt)-im - km*tt);

// Bound Excimer
// determine Ibm iteratively
// number of terms to be summed up
```

```
double imMin = ceil(6+3*im);

// initialize
double Ibe = 0;
double ifac = 1;
double term1, term2, term3;
int ii;

// we start at ii=1 because summand is 0 for ii=0
for(ii = 1; ii < imMin; ii++ )
{
       ifac *= ii; //Factorial j!
       term1= pow(im,ii)/ifac;
       term2= ((ii*KeV)/(1+ii*KeV-ke/km));
       term3= (exp(-ke*tt) - exp(-km*(1 +KeV*ii)*tt));
       Ibe += term1 * term2 * term3; //excimer sum
}
Ibe*= Xb*exp(-im); // complete equation

// Total decay
It = I0 + As*exp(-tt/ts) + Af*If + Abm*Ibm + Abe*Ibe;
```

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*.

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

```
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*.

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

```
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));
```