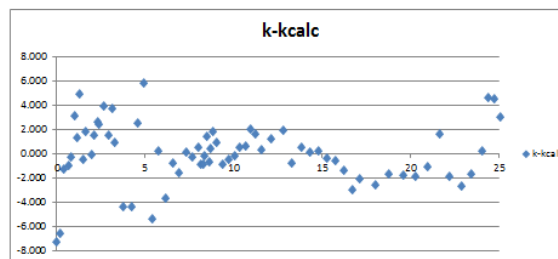
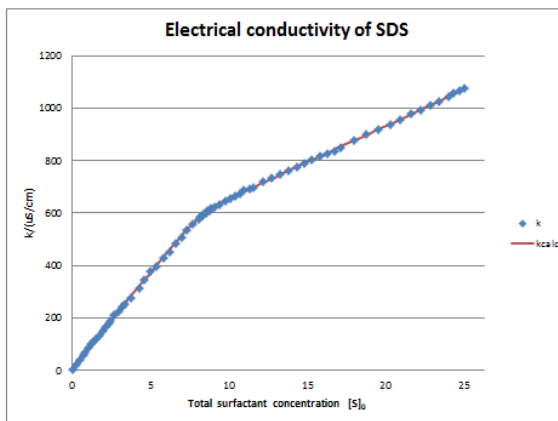


Experimental Data		Calculated	Differences for Solver		Parameter	
S0/mM	k	kcalc	k-kcalc	(k-kcalc)^2	cmc	
mM	uS/cm	uS/cm	uS/cm		r	0.128
0	3.5	10.78	-7.284	53.058	a	72.5
0.20	18.7	25.23	-6.533	42.677	b	27.7
0.40	38.3	39.57	-1.267	1.605	c	10.8
0.69	59.9	60.86	-0.956	0.914		
0.79	67.6	67.30	-0.296	0.088	ChiSqr	428.950
0.98	85	81.89	3.106	9.645		
1.17	97.1	95.78	1.317	1.734		
1.27	107.6	102.69	4.913	24.139		
1.46	116	116.41	-0.414	0.171		
1.64	131.8	130.03	1.765	3.116		
1.92	150.2	150.27	-0.070	0.005		
2.11	165.1	163.63	1.470	2.160		
2.29	179.5	176.89	2.611	6.817		
2.38	185.9	183.48	2.420	5.854		
2.65	207	203.11	3.895	15.171		
2.92	224	222.51	1.492	2.226		
3.10	239	235.32	3.678	13.529		
3.27	249	248.04	0.960	0.922		
3.70	275	279.42	-4.423	19.561		
4.21	312	316.32	-4.323	18.689		
4.55	343	340.47	2.526	6.379		
4.95	376	370.17	5.834	34.031		
5.36	394	399.30	-5.303	28.118		
5.75	428	427.85	0.150	0.023		
6.14	452	455.72	-3.716	13.812		
6.52	482	482.72	-0.721	0.520		
6.90	507	508.57	-1.573	2.475		
7.26	533	532.89	0.108	0.012		
7.63	555	555.28	-0.276	0.076		
7.98	576	575.41	0.590	0.348		
8.12	582	582.79	-0.795	0.631		
8.26	589	589.80	-0.796	0.634		
8.33	593	593.16	-0.155	0.024		
8.47	601	599.60	1.403	1.968		
8.61	605	605.68	-0.684	0.468		
8.68	609	608.60	0.400	0.160		
8.81	616	614.19	1.807	3.265		
9.02	623	622.03	0.971	0.942		

□



APNMODEL

FITTING-FUNCTIONS

FOR MICROSOFT EXCEL

WAJIH AL-SOUFI*, LUCAS PIÑEIRO, AND MERCEDES NOVO

DEPARTMENT OF PHYSICAL CHEMISTRY, FACULTY OF SCIENCE,
UNIVERSITY OF SANTIAGO DE COMPOSTELA, E-27002 LUGO, SPAIN.

wajih.al-soufi@usc.es

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

CONTENTS

Licence	3
Change History	3
Use in Microsoft Excel Worksheets	4
Installation as Excel Add-in	4
Examples.....	5
Concentrations.....	5
Electrical Conductivity (indirect)	5
Electrical Conductivity (direct)	6
Nonlinear Fit of experimental electrical conductivity data – cmc determination	6
Nonlinear Fit of experimental surface tension data – cmc determination	7
Fitting functions for Excel	8
Concentration Model	8
APNS1	8
Surfactant Properties	8
APNConductivity	8
Utility functions.....	9

LICENCE



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Please cite the following article:

1. 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](https://doi.org/10.1016/j.jcis.2011.12.037)

More information in

2. 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](https://doi.org/10.1039/c3sm52092g)
3. 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.jcis.2014.10.010](https://doi.org/10.1016/j.jcis.2014.10.010)

CHANGE HISTORY

V1.1	2015-10-17	Definition
V2.1	2017-11-17	Use as Excel Add-Ins. Improve description. Excel 2016 Surface tension

USE IN MICROSOFT EXCEL WORKSHEETS

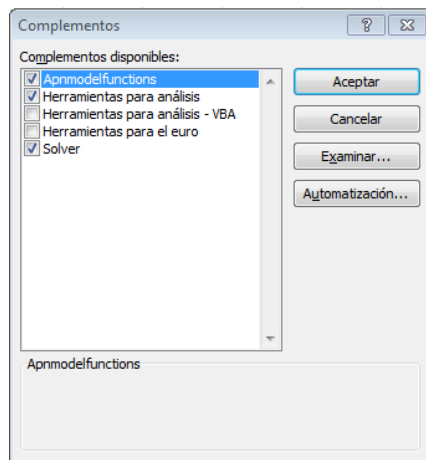
We provide here the model functions for **Microsoft Excel**. They can be used for **nonlinear fitting (Solver)** and for calculations in columns or other functions. Once installed as Excel Add-Ins they can be used in Excel cells together with the built-in functions. The functions will appear in the category “user defined functions”.

We tested the functions with Excel 2010 and Excel 2016. We implemented the functions in Visual Basic.

INSTALLATION AS EXCEL ADD-IN

Here’s how to install the model functions in Excel as Add-ins:

1. Download the Add-in **APNModel_Excel_Add-In.xlam** to a directory on your PC. You can choose any directory, however, don’t rename, move or delete this file once installed.
2. **Excel 2010:** click the **Microsoft Office Button**, click **Options**
Excel 2016: click the **File tab**, click **Options**
3. In the **Excel Options** dialog box, click the **Add-Ins** category.
4. In the **Manage** box, click **Excel Add-ins**, and then click **Go**.
5. The Add-Ins dialog box appears.
6. If the add-in “Apmmodelfunctions” is not yet listed, click on **Browse** and select the file **APNModel_Excel_Add-In.xlam** (this has an .xlam extension!) you downloaded.
Allow Excel to copy the add-in to the default location (add-in folder).
7. In the **Add-Ins available** box, select the check box beside **Apmmodelfunctions**, as shown below.
8. Select also the check box beside **Solver**



After these steps, our custom functions will be available in the **User Defined** category in the **Insert Function** dialog box.

Please report any problems to wajih.al-soufi@usc.es

EXAMPLES

We describe examples of the use of the APN-model in the Excel-File **APNModelFunctions_Excel_Example_V2_2.xlsx**

CONCENTRATIONS

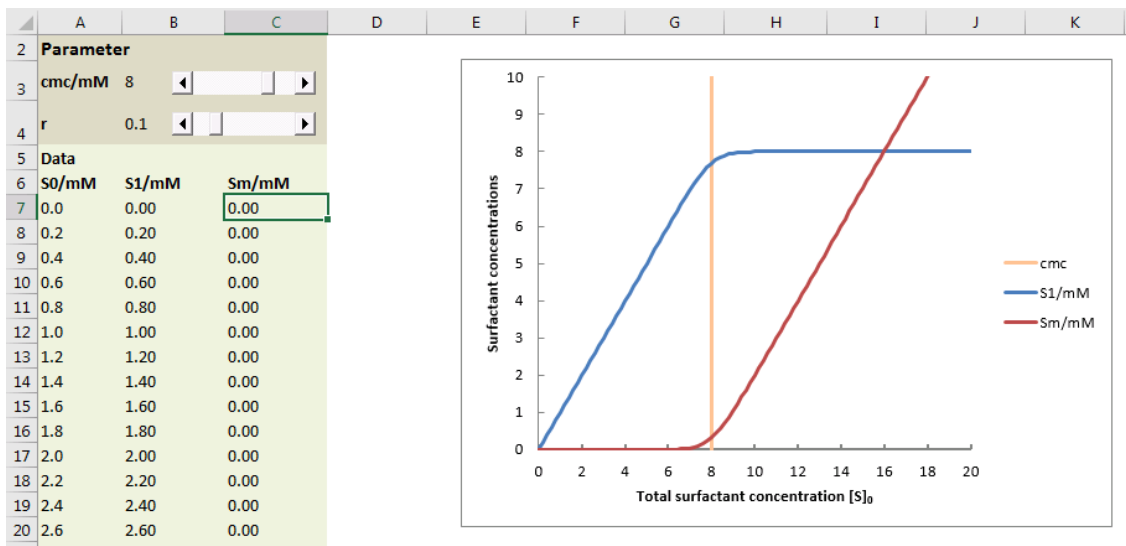
On the first worksheet **APN-Concentrations** we calculate the concentrations of monomeric $[S1]$ and micellized $[Sm]$ surfactant for a given interval of the total concentration $[S0]$.

Range A2-C4 **Parameters**: the values of cmc (B3) and r (B4) can be changed moving the sliders in C3 and C4.

Column A **Data**: values of the total surfactant concentration, $[S0]$.

Column B **S1/mM**: concentration of **monomeric surfactant**, $[S1]$ calculated with the the APN-Function "**=APNS1(cS0,cmc,r)**". For cS0 the corresponding value of $[S0]$ from the first column (A7) is used. The parameters **cmc** and **r** are taken form the cells B3 and B4, **=APNS1(A7;\$B\$3;\$B\$4)**

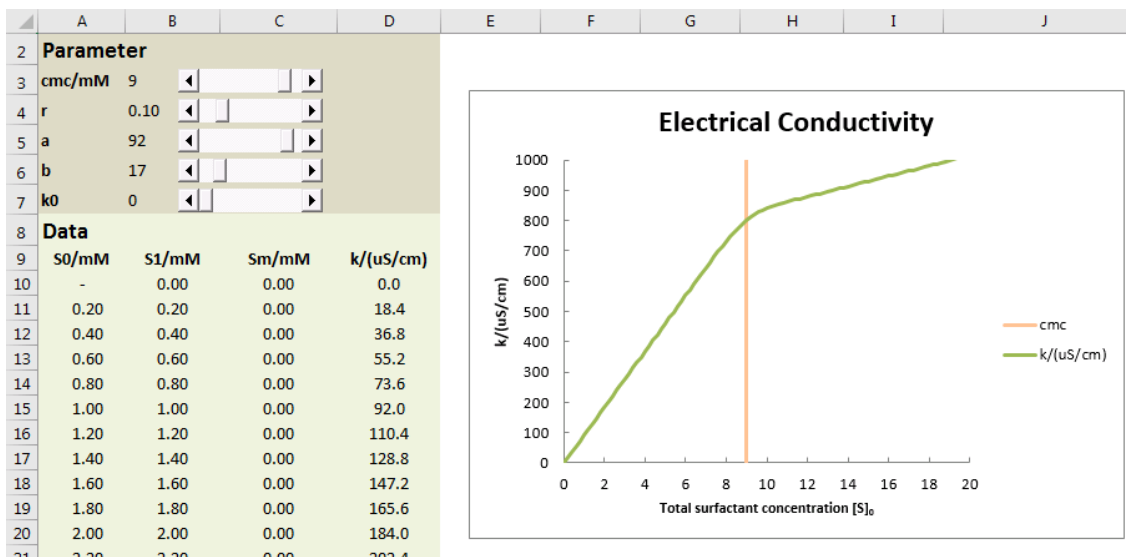
Column C **Sm/mM**: concentration of micellized $[Sm]$ surfactant $[Sm]=[S0]-[S1]$, **=A7-B7**



ELECTRICAL CONDUCTIVITY (INDIRECT)

On the second worksheet **APN-Conductivity (indirect)** we calculate the electrical conductivity κ of a surfactant solution as a function of the cmc, the relative transition width r , the slopes a and b , and the residual solvent conductivity κ_0 for a given interval of the total concentration $[S0]$.

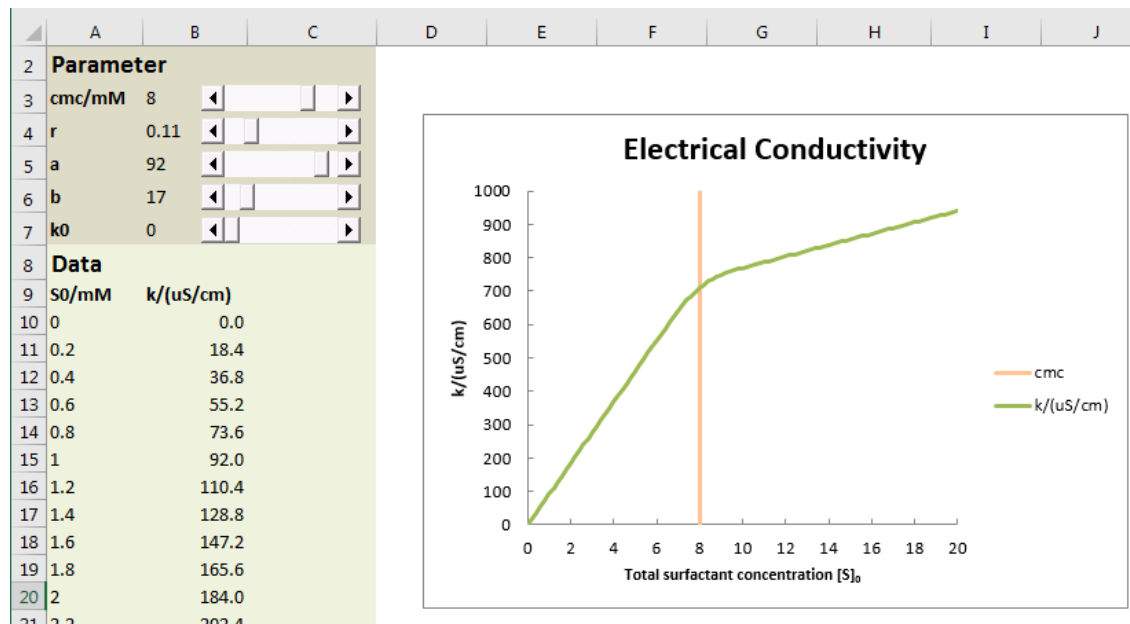
We first calculate the concentrations $[S1]$ and $[Sm]$ as described for the first worksheet. Then we calculate the conductivity as $\kappa = a [S1] + b [Sm] + \kappa_0$ with the parameters given in B3-B7.



ELECTRICAL CONDUCTIVITY (DIRECT)

The third worksheet APN-Conductivity (direct) is similar to the second one, however, here we calculate the electric conductivity κ directly from [S0] using the APN-Function “= APNConductivity(cS0,cmc,r,a,b,c)”.

APNConductivity(cS0,cmc,r,a,b,c) calculates the electrical conductivity κ of a surfactant solution as a function of the cmc, the relative transition width r, the slopes a and b, and the residual solvent conductivity $c=k_0$ for a given interval of the total concentration [S0] as $\kappa = a [S1] + b [Sm] + c$.



NONLINEAR FIT OF EXPERIMENTAL ELECTRICAL CONDUCTIVITY DATA – CMC DETERMINATION

In the fourth worksheet, we demonstrate how to fit experimental data of the electric conductivity κ of a surfactant with the APN-Model in order to determine the cmc with high precision.

The electrical conductivity data of SDS is described in the publication Al-Soufi et. al 2012 cited above.

We fit the data with the APN-Function for the electric conductivity κ “= APNConductivity(cS0,cmc,r,a,b,c)” as a function of the experimental surfactant concentration [S0] and the parameters cmc,r,a,b,c:

$$\kappa = a [S1] + b [Sm] + c$$

Columns A and B contain the experimental data.

In columns C we calculate the conductivity data with the APN-function “APNConductivity(cS0,cmc,r,a,b,c)” and some starting values of the parameter given in cells G4-G8.

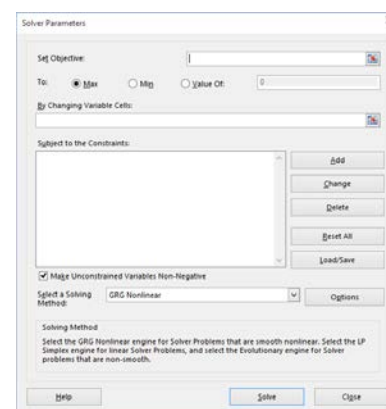
Columns D and E contain the error (difference) between experimental and calculated conductivity values and their squared values.

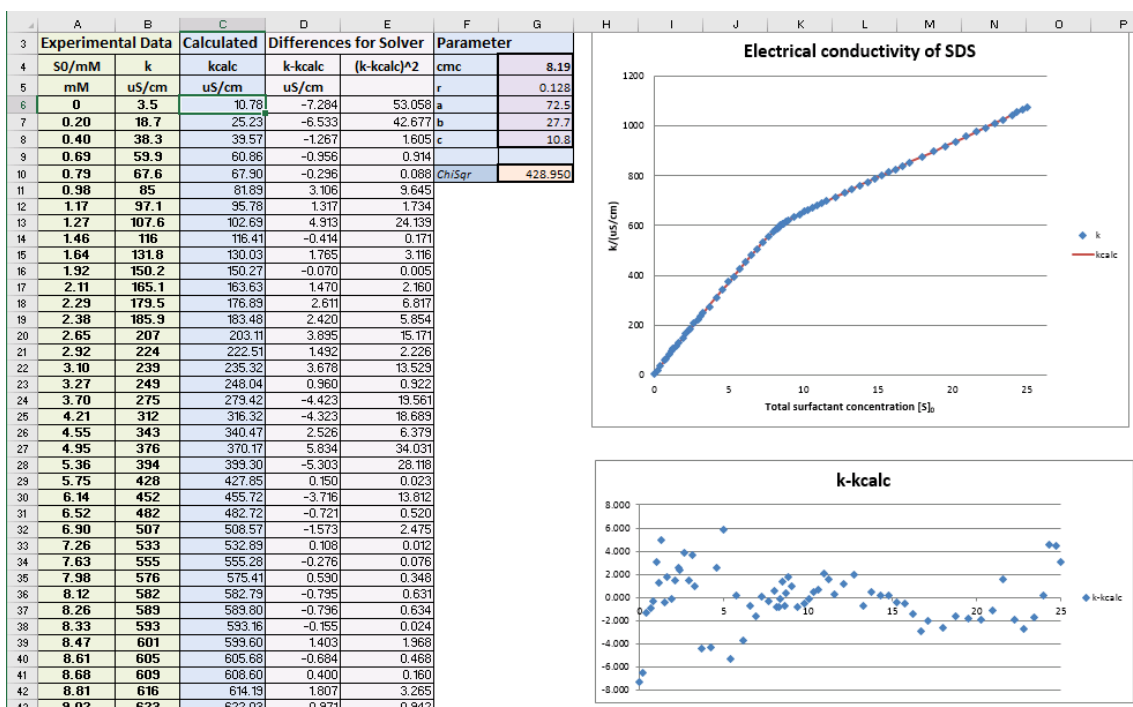
Cell G10 contains the sum of squared errors (SSE, χ^2): “=SUM(E6:E75)”

We then use **Excel Solver** for the nonlinear fit. On the **Data** tab, in the **Analysis** group, click **Solver...** (Solver is an add-in, if you cannot find it, you have to activate it as described at the beginning of this document).

In the **Solver Window**

1. **Set objective** to the SSE in G10
2. Select **Min** in order to minimize the SSE
3. **By changing variable cells** in G4:G8 (parameters to be optimized)
4. **Deselect** the option **Make Unconstrained Variables Non-Negative** in order to allow for negative values in the parameters.
5. Click **Solve**. This starts the fit. The result is directly given in the parameter cells G4-G8 of the worksheet.





NONLINEAR FIT OF EXPERIMENTAL SURFACE TENSION DATA – CMC DETERMINATION

In the fifth worksheet, we demonstrate how to fit experimental data of the surface tension γ of a surfactant with the APN-Model in order to extract the cmc.

The fit of the surface tension data of SDS is described in the publication Al-Soufi et. al 2012 cited above.

The surface tension data of SDS solutions at 20°C were obtained from Watanabe et al. (K. Watanabe, S. Niwa, Y.H. Mori, Journal of Chemical & Engineering Data. 50 (2005) 1672.)

In this case, we first calculate the monomer concentration $[S_1]$ for each experimental value of the total surfactant concentration using the function APNS1 as described before. Then we calculate the surface tension with the Szyszkowski equation $\gamma = \gamma_0 - a \ln(1 + K_{ad} \cdot [S_1])$

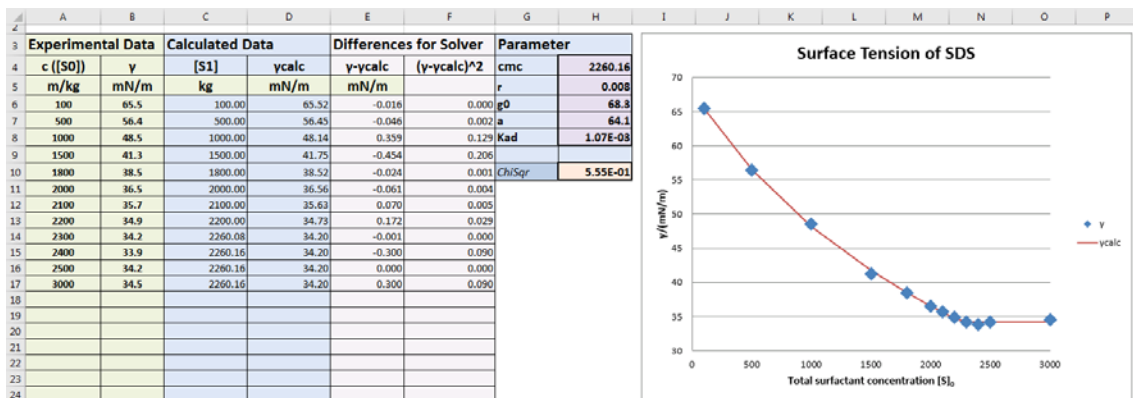
The parameters are the adsorption equilibrium constant K_{ad} , the surface tension of the solvent γ_0 , and a constant a . Then we fit the data with Excel Solver changing the parameters of APNS1 and the Szyszkowski equation.

Columns A and B contain the experimental data.

In column C we calculate the concentration of **monomeric surfactant, $[S_1]$** with the the APN-Function **"=APNS1(cS0,cmc,r)"** and cmc and r given in cells H4 and H5.

In column D we calculate then the surface tension with the Szyszkowski equation and the parameters γ_0 , a and K_{ad} in cells H6-H8. **"=SH\$6-SH\$7*LOG(1+SH\$8*C6)"**

Columns E and F contain the error its their squared values. Cell H10 contains the sum of squared errors (SSE, χ^2): **"=SUM(F6:F17)"**. Then we minimize the SSE with Excel Solver as described above.



FITTING FUNCTIONS FOR EXCEL

CONCENTRATION MODEL

APNS1

Concentration model used by all other derived properties.

Takes [S]0 and calculates the monomeric concentration [S1] as function of the cmc and the relative transition width r.

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

Use: =APNS1(cS0,cmc,r)
with
cS0 = total surfactant concentration [S]₀
cmc = critical micelle concentration
r = relative transition width
returns MONOMERIC CONCENTRATION [S₁]

```
Function APNS1(cS0 As Double, cmc As Double, r As Double) As Double
```

```
...
```

```
'Uses APNErf(x) for compatibility with older Excel versions
```

```
Dim s0 As Double, A As Double, Pi As Double
```

```
Pi = 3.14159265359 'constant pi
```

```
s0 = cS0 / cmc 'relative total concentration
```

```
A = 2 / (1 + Sqr(2 / Pi) * r * Exp(-1 / (2 * r * r))) + APNErf(1 / Sqr(2) / r) 'amplitude A
```

```
APNS1 = cmc * (1 - (A / 2) * (Sqr(2 / Pi) * r * Exp(-(s0 - 1) ^ 2 / (2 * r * r))) + (s0 - 1) * (APNErf((s0 - 1) / (Sqr(2) * r)) - 1)))
```

SURFACTANT PROPERTIES

APNCONDUCTIVITY

Conductivity of a surfactant solution.

Takes [S]0 and calculates the electric conductivity κ as function of the cmc, the relative transition width r and the slopes a and b, and the solvent conductivity c = ks.

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

This function needs the function APNModel_S1.

Use: = APNConductivity(cS0,cmc,r,a,b,c)
with
cS0 = total surfactant concentration [S]₀
cmc = critical micelle concentration
r = relative transition width
a = slope a (< cmc)
b = slope b (> cmc)
c = **SOLVENT CONDUCTIVITY C = K_s**
returns ELECTRIC CONDUCTIVITY K


```

Function APNConductivity(cS0 As Double, cmc As Double, r As Double, a As Double, b As Double, c
As Double) As Double
...
'Uses APNS1()

Dim cS1 As Double, cSm As Double

cS1 = APNS1(cS0, cmc, r)
cSm = cS0 - cS1

APNConductivity = a * cS1 + b * cSm + c

```

UTILITY FUNCTIONS

The function APNS1() needs APNErf(x), which defines the error function not included in older excel VBA versions.

```

Function APNErf(x As Double) As Double
'Source: http://www.johndcook.com/blog/2009/01/19/stand-alone-error-function-erf/
'Adapted to VBA Wajih Al-Soufi, 2015

'Wajih Al-Soufi, Universidad de Santiago de Compostela, Lugo, Spain, 2015
'http://www.usc.es/fotofqm/en/units/single-molecule-fluorescence/research/model-monomer-and-micellar-
concentrations-surfactant

Dim y As Double, Sign As Double, t As Double, p As Double
Dim a1 As Double, a2 As Double, a3 As Double, a4 As Double, a5 As Double

'Exception for small x : (Coment of Jason Merrill, 2015)
'one term of the Taylor series for erf(x) = 2/sqrt(pi)*x
If Abs(x) < 0.001 Then
    APNErf = 1.12837916709551 * x
Else

    'Constants
    a1 = 0.254829592
    a2 = -0.284496736
    a3 = 1.421413741
    a4 = -1.453152027
    a5 = 1.061405429
    p = 0.3275911

    'Save the sign of x
    Sign = 1
    If x < 0 Then
        Sign = -1
        x = Abs(x)
    End If

    'Abramowitz, Stegun 7.1.26
    t = 1 / (1 + p * x)
    y = 1 - (((((a5 * t + a4) * t) + a3) * t + a2) * t + a1) * t * Exp(-x * x)

    APNErf = Sign * y
End If
End Function

```