Equations for determining rate constants from CD data

The following are simple equations in SigmaPlot "fit" file format for finding the rates of folding for first, second and third order reactions.

I. First order reaction. In these equations the rate constant, in units of s^{-1}, is independent of the units of the dependent variable.

```
 [Parameters]


a=1; maximum fraction folded - this can be change to ellipticity of fully folded protein, maximal
;fluorescence or absorbance change
b=5e-3 ; folding constant

 [Variables]
v=col(1)   ; independent variable time
w=col(2)   ; dependent variable, fraction folded, CD signal, absorbance, fluorescence etc

[Equations]

f=a*(1-exp(-b*x)); first order rate equation
fit f to y


[Constraints]
b>0
[Options]
tolerance=0.000100
stepsize=100
iterations=100
```

II Second order reaction. If the dependent variable, y, is not expressed as the molar concentration of folded protein, the apparent rate constant must be divided by the protein concentration to determine the rate constant in $L \cdot mol^{-1} \cdot s^{-1}$.

```
[Variables]
t = col(1) ; time
y = col(2); fractional ellipticity change, ellipticity change, absorption change or fluorescence
change

[Parameters]

a = 1 ; maximal change - change to the value when the protein is completely folded
b = 0.01 ; initial estimate of the rate constant of folding
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```
[Equation]
q=1/a + b*t ; 2nd order rate equation.
A=(1/q)
f=a-A ; change in fraction folded, ellipticity etc
fit f to y

[Constraints]
a < 1; maximal change is constrained to be less than value observed when protein is fully folded
[Options]
tolerance=1e-10
stepsize=100
iterations=100
```

III. Third order reaction. If the dependent variable, y, is not expressed initially as the concentration of folded protein, the apparent rate constant must be divided by the square of initial protein concentration to determine the rate constant in L^{2} ·.$mol^{-2\cdot}s^{-1}$

```
[Variables]
t = col(1); time
y = col(2); fraction folded, ellipticity, absorbance or fluorescence change, conc of folded protein

[Parameters]
a = 1 ; maximal fraction folded
b = 0.02; apparent rate constant

[Equation]
q=1/a^2 +b*t
A=sqrt(1/q)
B=a-A
fit B to y

[Constraints]
a < 1; maximal change less than value when fully folded

[Options]
tolerance=0.000100
stepsize=100
iterations=100
```