Supplementary Material (ESI) for Metallomics

Supporting Information for: Copper (I) and copper (II) binding to β-amyloid 16 (Aβ16) studied by electrospray ionization mass spectrometry

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The simulated curves representing the time evolution of the concentrations of Cu(I)- and Cu(II)-Aβ complexes, Cu^{2+} and Aβ were calculated based on empirical chemical kinetics. The static state approximation was applied to this kinetic model *i.e.* the concentration of Cu^{+} maintained constant during the whole process and the rate equations including all the concentrations of Cu(I)- and Cu(II)-Aβ complexes, Cu^{2+}, Cu^{+}, and Aβ were then given as below:

$$\frac{d[\mathrm{Cu^I-A}\beta]}{\mathrm{dt}} = k_1[\mathrm{Cu^I}][\mathrm{A}\beta] + k_{\mathrm{red}}[AA][\mathrm{Cu^{II}-A}\beta]$$

$$\frac{d[\mathrm{Cu^{II}-A}\beta]}{\mathrm{dt}} = k_2[\mathrm{Cu^{II}}][\mathrm{A}\beta] - k_{\mathrm{red}}[AA][\mathrm{Cu^{II}-A}\beta]$$

$$\frac{d[\mathrm{Cu^{II}}]}{\mathrm{dt}} = k_{\mathrm{ox}}[\mathrm{Cu^I}] - k_2[\mathrm{Cu^{II}}][\mathrm{A}\beta]$$

$$\frac{d[\mathrm{Cu^{I}}]}{\mathrm{dt}} = k - k_{\mathrm{ox}}[\mathrm{Cu^I}] - k_1[\mathrm{Cu^I}][\mathrm{A}\beta] = 0$$

$$[\mathrm{Cu^I-A}\beta] + [\mathrm{Cu^{II}-A}\beta] + [\mathrm{A}\beta] = C_0$$

These equations could be applied to the both presence and absence of reducing agent in the peptide solution just dependent on the assignment of k_{red} as 0 or not. According to the assumption of the constant concentration of Cu^{+}, the stem of $[Cu^{I}]$ can be replaced by the expression of the combination of [Aβ], k and k_{ox}. Then the nonlinear system of ordinary differential equations including Cu(I)- and Cu(II)-Aβ complexes, Cu^{2+} and Aβ could finally be solved by Wolfram Mathematica 7.0.0. Here is the program written for the resolution of the dynamic equations ($j = k_1$, $p = k$, $l = k_{ox}$, k = k_2, $m = k_{red}$[AA]):

```
“Exit[]

system = {
   D[c1[t], t] == j*p/(1 + j*c4[t])*c4[t] + m*c2[t],
   D[c2[t], t] == k*c3[t]*c4[t] - m*c2[t],
   D[c3[t], t] == l*p/(1 + j*c4[t]) - k*c3[t]*c4[t],
   c1[t] + c2[t] + c4[t] == 10,
   c1[0] == c2[0] == c3[0] == 0
   };
param = {
   j -> 85,
   k -> 85,
   m -> 5,
   l -> 400,
   p -> 1.6
   };

delta=10/400; sol=NDSolve[system/.param,{c1[t],c2[t],c3[t],c4[t]},{t,0,10}];

timetable=Table[i*delta,{i,0,400}]//N;

Export["CuAB1.xls",
 Transpose[{timetable, sol[[1, 1, 2]] /. {t -> #} & /@ timetable}]]
Export["CuAB2.xls",
 Transpose[{timetable, sol[[1, 2, 2]] /. {t -> #} & /@ timetable}]]
Export["Cu2.xls",
 Transpose[{timetable, sol[[1, 3, 2]] /. {t -> #} & /@ timetable}]]
Export["AB.xls",
 Transpose[{timetable, sol[[1, 4, 2]] /. {t -> #} & /@ timetable}]]”.
```

Finally, the proper assignments of the rates constants to obtain the solution of the equations are given as follows: k = 1.6 μM·min^{-1}, $k_1 = k_2$ = 85 μM^{-1}·min^{-1}, k_{ox}= 400 min^{-1}, k_{red}[AA] = 5 min^{-1}. (j=k1, p=k, l=kox, k= k2, m=kred[AA])