APPENDIX II

Derivation of the rate equations of the two kinetic effects observed in the reaction between gold(III) and PADA in water

The slow effect
Between pH 4 and pH 6 the prevailing species derived from dissolution of tetrachloroaurate ion in water are the ternary complexes AuCl$_4^-$ and Au(OH)$_3$Cl$^-$. They are in equilibrium according to the reaction

$$
\text{Au(OH)}_3\text{Cl}^- + \text{Cl}^- \overset{K}{\rightleftharpoons} \text{AuCl}_4^- + \text{OH}^- \quad (\text{II.1})
$$

whose equilibrium constant is

$$
K = \frac{[\text{AuCl}_4^-][\text{OH}^-]}{[\text{Au(OH)}_3\text{Cl}^-][\text{Cl}^-]} \quad (\text{II.2})
$$

When PADA is added to an aqueous solution containing the gold(III) species shown in reaction (II.1) both species will react with PADA, but the extent of their contribution to the overall binding process will depend on the pH of the medium and on the chloride concentration.

For pH values less than 6.5 and for [Cl$^-] > 0.02$ M the main contribution to the overall reaction rate is provided by the species AuCl$_4^-$. Under these circumstances the reaction scheme will be

$$
\text{AuCl}_4^- + \underset{L}{\text{L}} \overset{k_1}{\rightleftharpoons} \text{Au(Cl)}_2^+\underset{L}{\text{L}} + 2\text{Cl}^- \quad (\text{II.3})
$$
where the first step, corresponding to reaction (II.1), is supposed to be fast with respect to the binding reaction (II.3). Note that the latter reaction is considered to be quantitative on the basis of the experimental results discussed in the text. The reaction rate can be expressed as the rate of disappearance of PADA, here denoted as $L$.

\[-d[L]/dt = k_1 [AuCl_4^-] [L]\]  \hspace{1cm} (II.4)

the mass conservation equation with respect to the metal is

\[C_{Au} = [AuCl_4^-] + [Au(OH)_3Cl^-] + [Au(Cl)_2L]\]  \hspace{1cm} (II.5)

The concentration of the species $Au(Cl)_2L$ cannot exceed the value of $C_L$, but, being $C_{Au} \gg C_L$, one can safely neglect it in the equation (II.5).

Introduction of equation (II.2) in (II.5) yields

\[[AuCl_4^-] = \frac{C_{Au}K[Cl^-]}{K[Cl^-] + [OH^-]}\]  \hspace{1cm} (II.6)

and introduction of equation (II.6) in (II.4) yields equation (II.7).

\[-\frac{d[L]}{dt} = \frac{k_1KC_{Au}[Cl^-]}{K[Cl^-] + [OH^-]} [L]\]  \hspace{1cm} (II.7)

Integration of equation (II.7), after variable separation, provides the expression for the time constant ($1/\tau$) of the binding process

\[\frac{1}{\tau} = \frac{k_1KC_{Au}[Cl^-]}{K[Cl^-] + [OH^-]}\]  \hspace{1cm} (II.8)

Equation (II.8) fit to the kinetics of the gold(III)-PADA system in water.
The Fast Effect

For pH values \( \geq 6.5 \) the contribution of \( \text{Au(OH)}_3\text{Cl}^- \) to the binding process can become observable while the contribution of \( \text{Au(OH)}_2\text{Cl}_2^- \) is reduced because of the higher \( \text{OH}^- \) concentration (see equation (II.13)). The biphasic effect observed at \( \text{pH} = 6.5 \) can be rationalized on such a ground. The fast phase and the corresponding kinetic effect can be represented by the reaction scheme below depicted.

\[
\begin{align*}
\text{Cl}^- + \text{Au(OH)}_3\text{Cl}^- & \quad \underset{K'}{\rightleftharpoons} \quad \text{Au(OH)}_2\text{Cl}_2^- + \text{OH}^- \\
\text{Au(OH)}_2\text{Cl}_2^- + \text{L} & \quad \underset{k_2}{\rightarrow} \quad \text{Au(OH)}_2^+ + \text{L} + 2\text{Cl}^- (\text{II.9})
\end{align*}
\]

The process belonging to the slow phase is not represented in the above scheme since the fast process is already completed when the slow process does start. The rate of the reaction in this case is represented by equation (II.10).

\[
-d[L-L]/dt = k_2[Au(OH)_3Cl^-][L-L] - k_2[Au(OH)_2L-L][Cl^-]^2 (\text{II.10})
\]

While the mass conservation equation, limited to the prevailing species, is:

\[
C_{\text{Au}} = [\text{Au(OH)}_2\text{Cl}_2^-] + [\text{Au(OH)}_3\text{Cl}^-] (\text{II.11})
\]

Introduction of equation (II.11) in the expression for \( K' \) yields equation (II.12).

\[
[Au(OH)_2Cl_2^-] = \frac{C_{\text{Au}}[\text{OH}^-]}{K'[\text{Cl}^-] + [\text{OH}^-]} (\text{II.12})
\]

The mass conservation equation with respect to the ligands

\[
C_L = [L-L] + [\text{Au(OH)}_3\text{L-L}] (\text{II.13})
\]
where Au(OH)\(_3\)L is an intermediate formed in the first process. Since the fast phase corresponds to an equilibrium process, equation (II.10) can be rewritten as equation (II.14)

\[
-d\delta[L-L]/dt = k_2[Au(OH)_2Cl_2^-]\delta[L-L] - k_2^{-2}[Cl^-]^2\delta[Au(OH)_3L-L]
\]  

(II.14)

where \(\delta[L]\) and \(\delta[Au(OH)_3L]\) indicate the shift of the respective species from the equilibrium position. Differentiation of equation (II.13) yields equation (II.15)

\[
\delta[L-L] + \delta[Au(OH)_3L-L] = 0
\]  

(II.15)

Introduction of equation (II.15) into equation (II.14) yields equation (II.16).

\[
-d\delta[L-L]/dt = \{k_2[Au(OH)_2Cl_2^-] \delta[L-L] + k_2^{-2}[Cl^-]^2\} \delta[L-L]
\]  

(II.16)

Introduction of equation (II.10) in equation (II.16) yields equation (II.17).

\[
\frac{-d\delta[L-L]}{dt} = \left[\frac{k_2C_{Au}[OH^-]}{K[Cl^-]+[OH^-]} + k_2^{-2}[Cl^-]^2\right] \delta[L-L]
\]  

(II.17)

Variable separation and integration of equation (II.17) yields the expression of the time constant of the fast process.

\[
\frac{1}{\tau_f} = \frac{k_2C_{Au}[OH^-]}{K[Cl^-]+[OH^-]} + k_2^{-2}[Cl^-]^2
\]  

(II.18)