APPENDIX IV

Derivation of the rate equation for the two kinetic effect observed in the reaction between gold(III) and PADA in SDS

The slow effect
Between pH 4 and 6 the Au(III) species prevailing on Au(OH)Cl$_3^-$ and Au(OH)$_2$Cl$_2^-$ . These species are repelled by the negatively charged SDS micelles. So, one can reasonably suppose that the species distribution in SDS is the same as in pure water. Therefore, the reactions taking place are

$$\begin{align*}
\text{Au(OH)$_2$Cl$_2^-$} + \text{Cl}^- & \rightleftharpoons K \text{Au(OH)Cl$_3^-$} + \text{OH}^- & (\text{IV.1}) \\
\text{Au(OH)Cl$_3^-$} + \text{L} & \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \text{Au(OH)Cl$_2^+$} + 2\text{Cl}^- & (\text{IV.2}) \\
\text{Au(OH)$_2$Cl$_2^-$} + \text{L} & \overset{k_2}{\underset{k_{-2}}{\rightleftharpoons}} \text{Au(OH)$_2$Cl$_2^+$} + \text{Cl}^- + \text{OH}^- & (\text{IV.3})
\end{align*}$$

Note that, differently from water, here the experiments indicate that the reverse steps are operative as well.

Under conditions of pseudo first-order, i.e. $C_{Au} \geq 10 \times C_{PADA}$, the concentrations of the Au(III) species can be expressed as a function of the total gold(III) concentration, $C_{Au}$, using the relationships

$$C_{Au} = [\text{Au(OH)Cl$_3^-$}] + [\text{Au(OH)$_2$Cl$_2^-$}] \quad (\text{IV.4})$$

and

$$\frac{[\text{Au(OH)Cl$_3^-$}]}{[\text{Au(OH)$_2$Cl$_2^-$}]} = K \frac{[\text{Cl}^-]}{[\text{OH}^-]} \quad (\text{IV.5})$$
Appendix IV

Introduction of equation (IV.5) to equation (IV.4) yields:

\[
[Au(OH)Cl_3^-] = \frac{K[Cl^-]C_{Au}}{K[Cl^-]+[OH^-]} \quad (IV.6)
\]

\[
[Au(OH)_2Cl_2^-] = \frac{[OH^-]C_{Au}}{K[Cl^-]+[OH^-]} \quad (IV.7)
\]

The relationship between the free ligand and the bound ligand is obtained using the mass conservation equation of the ligand is differential form.

\[\delta[L - L] + \delta[Au(OH)ClL^+] = 0 \quad (IV.8)\]

where \(\delta[i]\) represents the departure of the \(i\)th species from equilibrium. Express the rate of reaction as the rate of ligand disappearance:

\[
-\frac{d\delta[L - L]}{dt} = \left\{k_1[Au(OH)Cl_3^-] + k_2[Au(OH)_2Cl_2^-]\right\}\delta[L - L] - \left\{k_{-1}[Cl^-] + k_{-2}[OH^-]\right\}[Cl^-] \times \delta[Au(OH)ClL^+] \quad (IV.9)
\]

Introduction of equations (IV.4) and (IV.7) in to equation (IV.9) yields:

\[
-\frac{d\delta[L - L]}{dt} = \left\{k_1K[Cl^-][OH^-] + k_2[OH^-]\right\}C_{Au}\left\{k_{-1}[Cl^-] + k_{-2}[OH^-]\right\}[Cl^-] \delta[L - L] \quad (IV.10)
\]

Integration of equation (IV.10), after variable reparation yields the expression for the relaxation time of the slow process

\[
\frac{1}{\tau_s} = \left(\frac{k_1K[Cl^-]}{K[Cl^-]+[OH^-]} + \frac{k_2[OH^-]}{K[Cl^-]+[OH^-]}\right)C_{Au} + \left(k_{-1}[Cl^-] + k_{-2}[OH^-]\right)[Cl^-] \quad (IV.11)
\]
A plot of log \(k_d\) as pH of the data of Table 1 yields a straight line with a slope of 0.52 which indicate that \(k_d\) contains a term independent of \([\text{OH}^-]\) and a term proportional to \([\text{OH}^-]\), thus confirming equation (IV.11) as the most suitable to represent the experimental results.

**The fast effect**

Between pH 8.0 and 9.0 the main reacting species is \(\text{Au(OH)}_3\text{Cl}^-\) in equilibrium with a small amount if \(\text{Au(OH)}_3(\text{H}_2\text{O})\). Under these circumstance the most probable reactions are

\[
\text{Au(OH)}_3(\text{H}_2\text{O}) + \text{Cl}^- \rightarrow \text{K}
\]

\[
\begin{array}{c}
\text{Au(OH)}_3(\text{H}_2\text{O}) \\
\rightarrow
\end{array}
\]

\[
\text{Au(OH)}_3\text{Cl}^- + \text{H}_2\text{O}
\]

\[(\text{IV.12})\]

\[
\text{Au(OH)}_3(\text{H}_2\text{O}) + \text{L} \rightarrow \text{k}_1
\]

\[
\begin{array}{c}
\text{Au(OH)}_2^+ \\
\rightarrow
\end{array}
\]

\[
\text{Au(OH)}_2^+ \text{L}^- + \text{OH}^-
\]

\[(\text{IV.13})\]

The mass conservation equation with respect to gold(III) is

\[
C_{\text{Au}} = [\text{Au(OH)}_3(\text{H}_2\text{O})] + [\text{Au(OH)}_3\text{Cl}^-] + [\text{Au(OH)}_2^+ \text{L}^-]
\]

\[(\text{IV.14})\]

where the last term can be neglected because \(C_{\text{Au}} \geq 10 C_{\text{PADA}}\). The equilibrium constant of step (IV.12) can be written as

\[
\frac{[\text{Au(OH)}_3\text{Cl}^-]}{[\text{Au(OH)}_3(\text{H}_2\text{O})]} = \text{K}'[\text{Cl}^-]
\]

\[(\text{IV.15})\]

Introduction of equation (IV.15) into equation (IV.14) yields:

\[
[\text{Au(OH)}_3(\text{H}_2\text{O})] = \frac{C_{\text{Au}}}{1 + \text{K}'[\text{Cl}^-]}
\]

\[(\text{IV.16})\]

The mass conservation equation with respect to ligand, written in differential form
\(-\text{Appendix IV-}\)
\[
\delta[L - L] + \delta[\text{Au(OH)}_2 L_2] = 0
\]

The reaction rate can be written as
\[
- \frac{d\delta[L - L]}{dt} = k_1[\text{Au(OH)}_2 (\text{H}_2\text{O})]\delta[L - L] - k_{-1}[\text{OH}^-]\delta[\text{Au(OH)}_2 L_2]
\]

Integration of equation (IV.18), after variable separation, yields the reciprocal time constant:
\[
\frac{1}{\tau_s} = \frac{k_1 C_{\text{Au}}}{1 + K[\text{Cl}^-] + k_{-1}[\text{OH}^-]}
\]