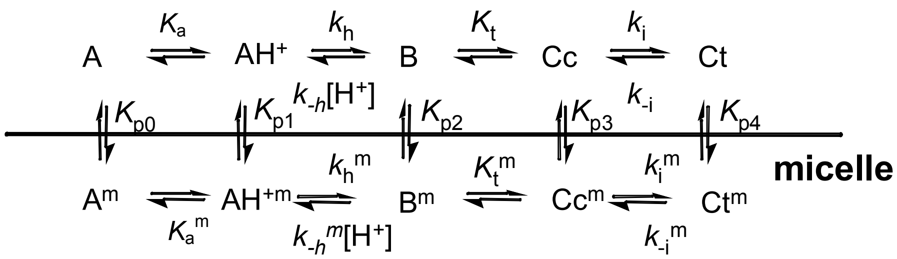
Supplementary Material

Deduction of the eqs. (12) and (18) according to Scheme 3 of the manuscript



- *Thermodynamic Equilibrium*

The total concentration of flavylium species is given by:

$$C_{AH^+} = [A] + [AH^+] + [B] + [Cc] + [Ct] + [A^m] + [AH^{+m}] + [B^m] + [Cc^m] + [Ct^m] \qquad \text{(S1)}$$

The concentration of each species can be expressed as a function of $[AH^+]$:

$$[AH^{+m}] = K_{p1}[AH^+] \qquad \text{(S2)}$$

$$[A] = \frac{K_a}{[H^+]}[AH^+] \qquad \text{(S3)}$$

$$[A^m] = K_{p0}\frac{K_a}{[H^+]}[AH^+] \qquad \text{(S4)}$$

$$[B] = \frac{K_h}{[H^+]}[AH^+] \qquad \text{(S5)}$$

$$[Cc] = K_t\frac{K_h}{[H^+]}[AH^+] \qquad \text{(S6)}$$

$$[Ct] = K_i K_t\frac{K_h}{[H^+]}[AH^+] \qquad \text{(S7)}$$

$$[B^m] = K_{p2}\frac{K_h}{[H^+]}[AH^+] \text{ or } [B^m] = K_{p1}\frac{K_h^{\ m}}{[H^+]}[AH^+] \qquad \text{(S8)}$$

$$[Cc^m] = K_{p3}K_t\frac{K_h}{[H^+]}[AH^+] \text{ or } [Cc^m] = K_{p1}K_t^{\ m}\frac{K_h^{\ m}}{[H^+]}[AH^+] \qquad \text{(S9)}$$

$$[Ct^m] = K_{p4}K_i K_t\frac{K_h}{[H^+]}[AH^+] \text{ or } [Ct^m] = K_{p1}K_t^{\ m}K_i^{\ m}\frac{K_h^{\ m}}{[H^+]}[AH^+] \qquad \text{(S10)}$$

Substituting eqs. (S2) to (S10) on eq. (S1) gives:

$$C_{AH^+}=\left[AH^+\right]\times\left(1+K_{p1}+\frac{K_a}{\left[H^+\right]}+K_{p0}\frac{K_a}{\left[H^+\right]}+\frac{K_h}{\left[H^+\right]}+K_t\frac{K_h}{\left[H^+\right]}+K_iK_t\frac{K_h}{\left[H^+\right]}+K_{p2}\frac{K_h}{\left[H^+\right]}+K_{p3}K_t\frac{K_h}{\left[H^+\right]}+K_{p4}K_iK_t\frac{K_h}{\left[H^+\right]}\right) \tag{S11}$$

.

or

$$C_{AH^+}=\left[AH^+\right]\times\left(1+K_{p1}+\frac{K_a}{\left[H^+\right]}+K_{p0}\frac{K_a}{\left[H^+\right]}+\frac{K_h}{\left[H^+\right]}+K_t\frac{K_h}{\left[H^+\right]}+K_iK_t\frac{K_h}{\left[H^+\right]}+K_{p1}\frac{K_h{}^m}{\left[H^+\right]}+K_{p1}K_t{}^m\frac{K_h{}^m}{\left[H^+\right]}+K_{p1}K_t{}^mK_i{}^m\frac{K_h{}^m}{\left[H^+\right]}\right) \tag{S12}$$

Mole fractions can therefore be taken using eqs. (S11) and (S12):

$$\chi_{AH^+}=\frac{\left[AH^+\right]}{C_{AH^+}}=\frac{\left[H^+\right]}{\left(\left(1+K_{p1}\right)\left[H^+\right]+K_a+K_{p0}K_a+K_h+K_tK_h+K_iK_tK_h+K_{p2}K_h+K_{p3}K_tK_h+K_{p4}K_iK_tK_h\right)} \tag{S13}$$

or

$$\chi_{AH^+}=\frac{\left[AH^+\right]}{C_{AH^+}}=\frac{\left[H^+\right]}{\left(\left(1+K_{p1}\right)\left[H^+\right]+K_a+K_{p0}K_a+K_h+K_tK_h+K_iK_tK_h+K_{p1}K_h{}^m+K_{p1}K_t{}^mK_h{}^m+K_{p1}K_t{}^mK_i{}^mK_h{}^m\right)} \tag{S14}$$

Since K_{p1}~0, because AH^+ resides in the bulk due to the electrostatic repulsion, eq. (S13) can be simplified to:

$$\chi_{AH^+}=\frac{\left[AH^+\right]}{C_{AH^+}}=\frac{\left[H^+\right]}{\left(\left[H^+\right]+K'^m_a\right)} \tag{S15}$$

$$K'^m_a=K'_a+K_{p0}K_a+K_{p2}K_h+K_{p3}K_hK_t+K_{p4}K_hK_tK_i \tag{S16}$$

or

$$K'^m_a=K'_a+K_{p0}K_a+K_{p1}K_h{}^m+K_{p1}K_t{}^mK_h{}^m+K_{p1}K_t{}^mK_i{}^mK_h{}^m \tag{S17}$$

where

$$K'_a=K_a+K_h+K_hK_t+K_hK_tK_i \tag{S18}$$

It is known that K'_a=8.9x10^{-4} M and K'^m_a=10$^{0.16}$ M, therefore K'_a can be neglected from the calculations. Also all species that are not AH^+ or Ct are not present in significant quantities at equilibrium, therefore the terms that come from A, B and Cc species (in the bulk and in the micellar phase) may be neglected. The only term that remains is therefore $K_{p4}K_hK_tK_i$ or $K_{p1}K_t^mK_i^mK_h^m$. It turns out that the product $K_hK_tK_i$ is known from experiments in water, and therefore the following relation can be used:

$$K'^m_a = K_{p4} K_h K_t K_i \tag{S19}$$

as seen in the text.

- *Thermal kinetics*

The kinetics of the thermal part follows a similar route of thinking. The only detectable species are, again, AH^+ and Ct. But the intermediate species should play a role as well. The sum of the intermediate species X may be given by:

$$[X] = [B] + [B^m] + [Cc] + [Cc^m] \tag{S20}$$

Assuming that these species are in fast equilibrium, one obtains the following differential equations:

$$\begin{aligned}\frac{d([AH^+]+[A])}{dt} &= -k_h \frac{[H^+]}{[H^+]+K_a}([AH^+]+[A]) + k_{-h}[H^+][B] + k_{-h}^m[H^+][B_m] \\ &= -k_h \frac{[H^+]}{[H^+]+K_a}([AH^+]+[A]) + (k_{-h}\chi'_B + k_{-h}^m \chi'_{B^m})[H^+][X]\end{aligned} \tag{S21}$$

which accounts for the concentration change of flavylium species (AH^+ and A);

$$\begin{aligned}\frac{d[X]}{dt} &= k_h \frac{[H^+]}{[H^+]+K_a}([AH^+]+[A]) - k_{-h}[H^+][B] - k_{-h}^m[H^+][B^m] - k_i[Cc] - k_i^m[Cc^m] + k_{-i}^m[Ct^m] = \\ &= k_h \frac{[H^+]}{[H^+]+K_a}([AH^+]+[A]) - (k_{-h}[H^+]\chi'_B + k_{-h}^m \chi'_{B^m}[H^+] + k_i\chi'_{Cc} + k_i^m \chi'_{Cc^m})[X] + k_{-i}^m[Ct^m]\end{aligned} \tag{S22}$$

which accounts for the concentration change of intermediate species (B, B^m, Cc and Cc^m), and;

$$\frac{d([Ct]+[Ct^m])}{dt} = k_i[Cc] + k_i^m[Cc^m] - k_{-i}^m[Ct^m] = (k_i\chi'_{Cc} + k_i^m\chi'_{Cc^m})[X] - k_{-i}^m[Ct^m] \tag{S23}$$

which accounts for the concentration change of *trans*-chalcone species (Ct and Ct^m). Since K_{p4} is very large, the concentration of Ct may be neglected.

Applying the steady-state approximation for eq. (S22), one obtains:

$$[X]=\frac{k_h\frac{[H^+]}{[H^+]+K_a}([AH^+]+[A])+k_{-i}^m[Ct^m]}{k_{-h}[H^+]\chi'_B+k_{-h}^m\chi'_{B^m}[H^+]+k_i\chi'_{Cc}+k_i^m\chi'_{Cc^m}} \tag{S24}$$

Substituting [X], one obtains:

$$\frac{d([AH^+]+[A])}{dt}=-k_h\frac{[H^+]}{[H^+]+K_a}([AH^+]+[A])+(k_{-h}\chi'_B+k_{-h}^m\chi'_{B^m})[H^+]\frac{k_h\frac{[H^+]}{[H^+]+K_a}([AH^+]+[A])+k_{-i}^m[Ct^m]}{k_{-h}[H^+]\chi'_B+k_{-h}^m\chi'_{B^m}[H^+]+k_i\chi'_{Cc}+k_i^m\chi'_{Cc^m}}=$$
$$=-\frac{k_h(k_i\chi'_{Cc}+k_i^m\chi'_{Cc^m})\frac{[H^+]}{[H^+]+K_a}}{k_{-h}[H^+]\chi'_B+k_{-h}^m\chi'_{B^m}[H^+]+k_i\chi'_{Cc}+k_i^m\chi'_{Cc^m}}([AH^+]+[A])+\frac{(k_{-h}\chi'_B+k_{-h}^m\chi'_{B^m})[H^+]k_{-i}^m[Ct^m]}{k_{-h}[H^+]\chi'_B+k_{-h}^m\chi'_{B^m}[H^+]+k_i\chi'_{Cc}+k_i^m\chi'_{Cc^m}}[Ct^m] \tag{S25}$$

$$\frac{d([Ct]+[Ct^m])}{dt}=(k_i\chi'_{Cc}+k_i^m\chi'_{Cc^m})\frac{k_h\frac{[H^+]}{[H^+]+K_a}([AH^+]+[A])+k_{-i}^m[Ct^m]}{k_{-h}[H^+]\chi'_B+k_{-h}^m\chi'_{B^m}[H^+]+k_i\chi'_{Cc}+k_i^m\chi'_{Cc^m}}-k_{-i}^m[Ct^m]$$
$$=\frac{k_h(k_i\chi'_{Cc}+k_i^m\chi'_{Cc^m})\frac{[H^+]}{[H^+]+K_a}}{k_{-h}[H^+]\chi'_B+k_{-h}^m\chi'_{B^m}[H^+]+k_i\chi'_{Cc}+k_i^m\chi'_{Cc^m}}([AH^+]+[A])-\frac{(k_{-h}\chi'_B+k_{-h}^m\chi'_{B^m})[H^+]k_{-i}^m[Ct^m]}{k_{-h}[H^+]\chi'_B+k_{-h}^m\chi'_{B^m}[H^+]+k_i\chi'_{Cc}+k_i^m\chi'_{Cc^m}}[Ct^m] \tag{S26}$$

The solution of the set of differential equations is now easy to achieve, and the observed rate constant for the first order kinetics is given by:

$$k_{thermal}=\frac{\frac{[H^+]}{[H^+]+K_a}k_h(\chi'_{Cc^m}k_i^m+k_i\chi'_{Cc})+k_{-i}^m(\chi'_Bk_{-h}+k_{-h}^mk_{-i}^m)[H^+]}{\chi'_{Cc^m}k_i^m+\chi'_Bk_{-h}[H^+]+k_i\chi'_{Cc}+k_{-h}^m\chi'_{B^m}}$$
$$=\frac{\frac{[H^+]}{[H^+]+K_a}k_hK_t(k_i+k_i^mK_{p3})+k_{-i}^m(k_{-h}+k_{-h}^mK_{p2})[H^+]}{K_t(k_i+k_i^mK_{p3})+(k_{-h}+k_{-h}^mK_{p2})[H^+]} \tag{S27}$$

as described in eq. (18) of the manuscript.