

NOTES ON MODELLING  
THE CHEMICAL SYSTEM IN  
MORROW ET AL. [NAT. COMM., 2019]  
& HOWLETT ET AL. [NAT. CHEM., 2022]

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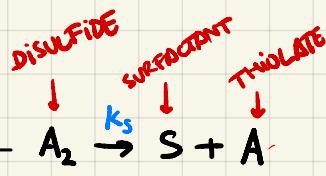
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## REACTIONS CONSIDERED

- SURFACTANT GENERATION

[SURFACE]  
SLOW



- OXIDATION

[BULK]  
SLOW



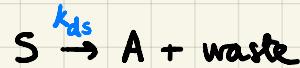
- DISSOCIATION OF OXIDANT

[BULK]  
FAST



- DISSOCIATION OF SURFACTANT

[SURFACE]  
(VERY) SLOW



- MICELLIZATION/DISSOCIATION OF MICELLES

[BULK]  
FAST



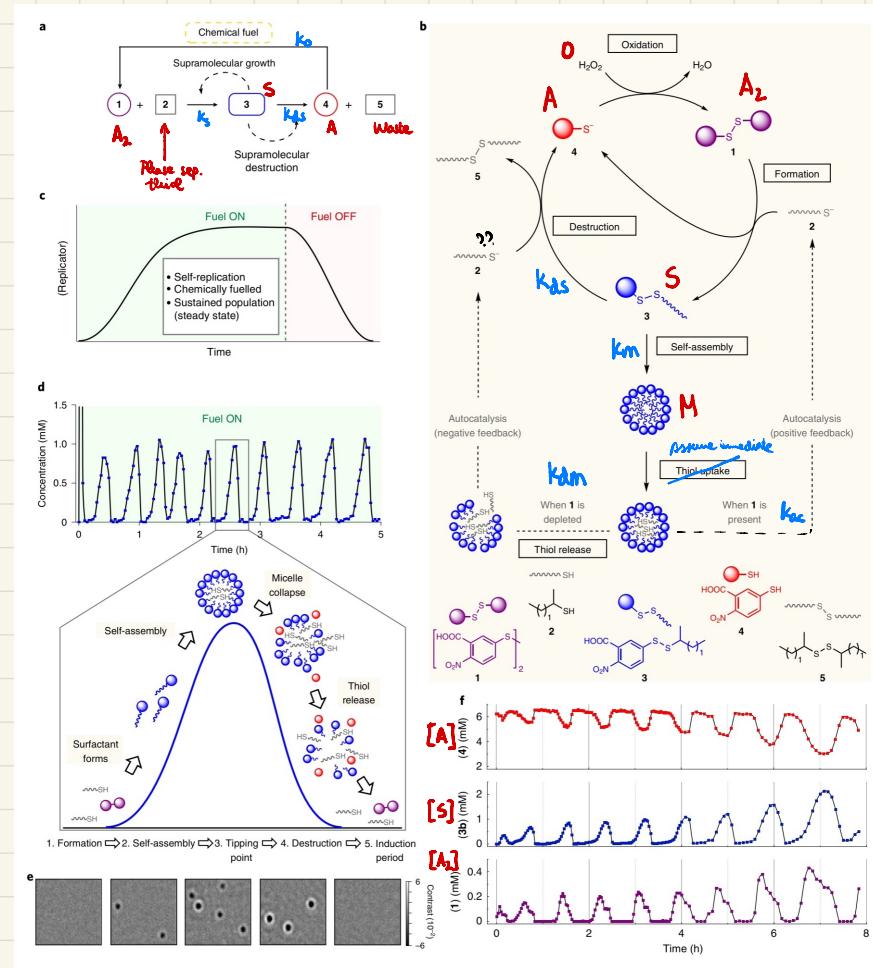
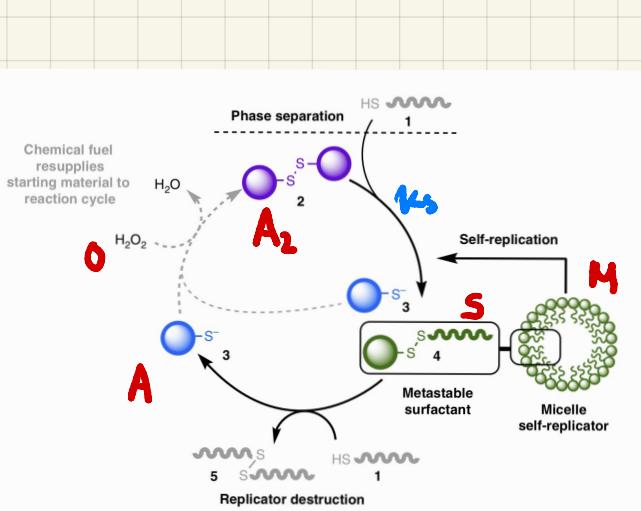
- AUTOCATALYTIC SURFACTANT GENERATION

[BULK]  
FAST



- AUTOCATALYTIC DISSOCIATION OF SURFACTANT

[BULK]  
FAST



## REACTION RATES

$$r_s = k_s C_{A_2} \quad r_{ds} = k_{ds} C_s$$

↑  
[1/s]

↑  
[1/s]

$$r_s^* = k_s^* C_M C_{A_2} \quad r_{ds}^* = k_{ds}^* C_M C_S$$

↑  
[m³/mol·s]

↑  
[m³/mol·s]

$$r_m = k_m C_S^\alpha \quad r_{dm} = k_{dm} C_M \quad r_o = k_o C_o C_A^2$$

↑  
[m³/mol²·s]

↑  
[1/s]

↑  
[m³/mol²·s]

$$r_{do} = k_{do} C_o$$

↑  
[1/s]

## MODEL EQUATIONS

In order to conserve mass in time:

$$\left. \begin{aligned} \frac{dc_A}{dt} &= r_o - r_s - r_s^* \\ \frac{dc_A}{dt} &= r_s + r_{ds} + r_s^* + r_{ds}^* - 2r_o \\ \frac{dc_o}{dt} &= r_{ext} - r_o - r_{do} \\ \frac{dc_s}{dt} &= r_s - r_{ds} + r_s^* - r_{ds}^* + n r_{dm} - n r_m \\ \frac{dc_m}{dt} &= r_m - r_{dm} \end{aligned} \right\}$$

Substituting the above rates we arrive at the final model:

$$\left. \begin{aligned} \frac{dc_A}{dt} &= k_o c_o c_A^2 - k_s c_{A_2} - k_s^* c_m c_{A_2} \\ \frac{dc_A}{dt} &= k_s c_{A_2} + k_s^* c_m c_{A_2} + k_{ds} c_s + k_{ds}^* c_m c_s - 2k_o c_o c_A^2 \\ \frac{dc_o}{dt} &= r_{ext} - k_o c_o c_A^2 - k_{do} c_o \\ \frac{dc_s}{dt} &= k_s c_{A_2} - k_{ds} c_s + k_s^* c_m c_{A_2} - k_{ds}^* c_m c_s + n k_{dm} c_m - n k_m c_s^\alpha \\ \frac{dc_m}{dt} &= k_m c_s^\alpha - k_{dm} c_m \end{aligned} \right\}$$

(all concentrations  
always in mole/m³)

For which we have the following initial conditions:

$$c_{A_2}(t=0) = C_{A_2} \quad c_A(t=0) = 0 \quad c_o(t=0) = 0 \quad c_s(t=0) = 0 \quad c_m(t=0) = 0$$

↑  
INITIALLY  
SUPPLIED CONCENTRATION  
OF DISULFIDE

←  
INITIALLY, NO SULFIDE, OXIDANT,  
SURFACTANT OR MICELLES

## MODEL REDUCTION

Benzene rings are conserved at all times. This can be seen by linear combination of the equations for  $C_A$ ,  $C_A'$ ,  $C_S$ ,  $C_M$  (the components with rings) to get:

$$2 \frac{dc_{A_2}}{dt} + \frac{dc_A}{dt} + \frac{dc_S}{dt} + n \frac{dc_M}{dt} = 0$$

which in turn means we can reduce the number of equations from 5 to 4:

$$\frac{d}{dt} (2C_{A_2} + C_A + C_S + nC_M) = 0$$

$$2C_{A_2} + C_A + C_S + nC_M = \text{constant}$$

$$2C_{A_2} + C_A + C_S + nC_M = 2C'_{A_2}$$

Substitute  
initial  
conditions

$c_A = 2(C'_{A_2} - c_{A_2}) - C_S - nC_M$

The reduced set of equations is then:

$$\frac{dc_{A_2}}{dt} = k_o c_0 [2(C'_{A_2} - c_{A_2}) - C_S - nC_M]^2 - k_s c_{A_2} - k_s^* c_M c_{A_2}$$

$$\frac{dc_S}{dt} = r_{ext} - k_o c_0 [2(C'_{A_2} - c_{A_2}) - C_S - nC_M]^2 - k_{ds} c_0$$

$$\frac{dc_M}{dt} = k_s c_{A_2} - k_{ds} c_S + k_s^* c_M c_{A_2} - k_{ds}^* c_M c_S + n k_{dm} c_M - n k_m c_S^m$$

$$\frac{dc_M}{dt} = k_m c_S^m - k_{dm} c_M$$

With initial conditions:

$c_{A_2}(t=0) = C'_{A_2}$

$c_0(t=0) = 0$

$c_S(t=0) = 0$

$c_M(t=0) = 0$

## CHARACTERISTIC SCALES

The CMC is given by the micellization / dissociation equilibrium:

$$r_m = r_{dm}$$

$$k_m \bar{C}_{cmc}^m = k_{dm} \left( \frac{\bar{C}_{cmc}}{n} \right)$$

$$\bar{C}_{cmc}^{m-1} = \frac{k_{dm}}{n k_m}$$

$$\boxed{\bar{C}_{cmc} = \left( \frac{k_{dm}}{n k_m} \right)^{\frac{1}{m-1}}}$$

We then nondimensionalize the equations as:

$$\left. \begin{array}{l} c_{A_2} \rightarrow \bar{c}_{A_2} c_{A_2} \\ c_0 \rightarrow \bar{c}_0 c_0 \\ c_s \rightarrow \bar{c}_{cmc} c_s \\ c_m \rightarrow \frac{\bar{c}_{cmc}}{n} c_m \\ t \rightarrow \tau t \end{array} \right\}$$

UNKNOWN

Which lead to :

$$\frac{\bar{c}_{A_2}}{\tau} \frac{dc_{A_2}}{dt} = k_0 \bar{c}_0 c_0 \left[ 2 \bar{c}_{A_2} (1 - c_{A_2}) - \bar{c}_{cmc} (c_s + c_m) \right]^2 - k_s \bar{c}_{A_2} c_{A_2} - k_s^* \frac{\bar{c}_{cmc}}{n} \bar{c}_{A_2} c_m c_{A_2}$$

$$\frac{\bar{c}_0}{\tau} \frac{dc_0}{dt} = r_{ext} - k_0 \bar{c}_0 c_0 \left[ 2 \bar{c}_{A_2} (1 - c_{A_2}) - \bar{c}_{cmc} (c_s + c_m) \right]^2 - k_{d0} \bar{c}_0 c_0$$

$$\frac{\bar{c}_{cmc}}{\tau} \frac{dc_s}{dt} = k_s \bar{c}_{A_2} c_{A_2} - k_{ds} \bar{c}_{cmc} c_s + k_s^* \frac{\bar{c}_{cmc}}{n} \bar{c}_{A_2} c_m c_{A_2} - k_{ds}^* \frac{\bar{c}_{cmc}}{n} \bar{c}_{cmc} c_m c_s - n k_m \bar{c}_{cmc} \bar{c}_s^m + n k_{dm} \frac{\bar{c}_{cmc}}{n} c_m$$

$$\frac{\bar{c}_{cmc}}{n \tau} \frac{dc_m}{dt} = k_m \bar{c}_{cmc} \bar{c}_s^m - k_{dm} \frac{\bar{c}_{cmc}}{n} c_m$$

The oxidant equation leads to a natural choice of  $\bar{C}_O$ :

$$\frac{dc_O}{dt} = \frac{\tau r_{ext}}{C_O} \left\{ 1 - \frac{k_O C_O \bar{C}_{A_2}^2}{r_{ext}} C_O \left[ 2(1 - c_{A_2}) - \left( \frac{C_{OMC}}{\bar{C}_{A_2}} \right) (c_S + c_M) \right]^2 - \frac{k_{dO} \bar{C}_O}{r_{ext}} C_O \right\}$$

NATURAL SCALE  
FOR OXIDANT  
CONCENTRATION

$$\bar{C}_O = \frac{r_{ext}}{k_O \bar{C}_{A_2}^2}$$

$$\frac{dc_O}{dt} = \underbrace{(\tau k_O \bar{C}_{A_2})}_{\text{Ref. time}} \left\{ 1 - C_O \left[ 2(1 - c_{A_2}) - \left( \frac{C_{OMC}}{\bar{C}_{A_2}} \right) (c_S + c_M) \right]^2 - \left( \frac{k_{dO}}{k_O \bar{C}_{A_2}^2} \right) C_O \right\}$$

Ref. time  
Two oxidation

For the disulfide:

$$\frac{dc_{A_2}}{dt} = \frac{\tau}{\bar{C}_{A_2}} \left\{ -k_S \bar{C}_{A_2} c_{A_2} - k_S^* \frac{C_{OMC}}{n} \bar{C}_{A_2} c_M c_{A_2} + \underbrace{k_O \bar{C}_O \bar{C}_{A_2}^2}_{r_{ext}} C_O \left[ 2(1 - c_{A_2}) - \left( \frac{C_{OMC}}{\bar{C}_{A_2}} \right) (c_S + c_M) \right]^2 \right\}$$

$$\frac{dc_{A_2}}{dt} = - \underbrace{(\tau k_S) c_{A_2}}_{\text{Hopefully slow}} - \underbrace{\left( \frac{\tau k_S^* C_{OMC}}{n} \right) c_M c_{A_2}}_{\text{Slow}} + \underbrace{\left( \frac{\tau r_{ext}}{\bar{C}_{A_2}} \right) C_O \left[ 2(1 - c_{A_2}) - \left( \frac{C_{OMC}}{\bar{C}_{A_2}} \right) (c_S + c_M) \right]^2}_{\text{We assume this is the dominant balance}}$$

For the surfactant:

$$\frac{dc_S}{dt} = \frac{\tau}{C_{OMC}} \left\{ k_S \bar{C}_{A_2} c_{A_2} - k_{ds} \bar{C}_{OMC} c_S + k_S^* \frac{C_{OMC}}{n} \bar{C}_{A_2} c_M c_{A_2} - k_{ds} \frac{C_{OMC}}{n} \bar{C}_{OMC} c_M c_S - n k_m \bar{C}_{OMC} c_S^m + k_{dm} \frac{C_{OMC}}{n} c_M \right\}$$

$$\frac{dc_S}{dt} = (\tau k_S) \left( \frac{\bar{C}_{A_2}}{C_{OMC}} \right) c_{A_2} - (\tau k_{ds}) c_S + \left( \frac{\tau k_S^* C_{OMC}}{n} \right) \left( \frac{\bar{C}_{A_2}}{C_{OMC}} \right) c_M c_{A_2} - \left( \frac{\tau k_{ds} C_{OMC}}{n} \right) c_M c_S - (\tau n k_m \bar{C}_{OMC}) c_S^m + (\tau k_{dm}) c_M$$

$$\frac{dc_S}{dt} = (\tau k_S) \left( \frac{\bar{C}_{A_2}}{C_{OMC}} \right) c_{A_2} - (\tau k_{ds}) c_S + \underbrace{\left( \frac{\tau k_S^* C_{OMC}}{n} \right) \left( \frac{\bar{C}_{A_2}}{C_{OMC}} \right) c_M c_{A_2} - \left( \frac{\tau k_{ds} C_{OMC}}{n} \right) c_M c_S - (\tau k_{dm}) [c_S^m - c_M]}_{\text{Assume dominant balance}}$$

3 body problem  
SOLVED DV

For the micelles:

$$\frac{dc_M}{dt} = \frac{n \tau}{C_{OMC}} \left\{ k_m \bar{C}_{OMC} c_S^m - k_{dm} \frac{C_{OMC}}{n} c_M \right\}$$

$$\frac{dc_M}{dt} = \tau n k_m \bar{C}_{OMC}^{m-1} \left\{ c_S^m - \frac{k_{dm}}{n k_m \bar{C}_{OMC}^{m-1}} c_M \right\}$$

$$\frac{dc_M}{dt} = (\tau k_{dm}) [c_S^m - c_M]$$

Ref. time  
Time of misc/demix  
[prob. large]

The slope is:

$$\frac{1}{k_0 \tilde{C}_{A_2}^2}, \frac{1}{k_{dm}} \ll \frac{n}{k_s^* \tilde{C}_{Auc}}, \frac{n}{k_{ds}^* \tilde{C}_{Auc}}, \frac{\tilde{C}_{A_2}}{r_{ext}} \ll \frac{1}{k_s}, \frac{1}{k_{ds}}$$

OXIDATION TIME      MICEDMIC TIME      AUTOCATL. SURFACTANT GENERATION TIME      AUTOCATLIC SURFACTANT DECOMPOSITION TIME      DISULFATE REGENSHMENT TIME      SURFACTANT GENERATION TIME      SURFACTANT DECOMPOSITION TIME

SURFACTANT DECOMPOSITION TIME

So we take  $\tau = \tilde{C}_{A_2}/r_{ext}$ . In the Nat. Comm. [plateau of surfactant]:

$$\tau = \frac{\tilde{C}_{A_2}}{r_{ext}} \approx \frac{20 \text{ mM}}{5 \frac{\mu\text{L}}{\text{hr}} \cdot 1.2 \text{ M} \cdot \frac{1}{5 \text{ mL}}} = \frac{20 \cdot 10^{-3} \frac{\text{mM}}{\text{L}}}{5 \cdot 10^{-5} \frac{\text{L}}{\text{hr}} \cdot 1.2 \frac{\text{mol}}{\text{L}} \cdot \frac{1}{5 \cdot 10^{-3} \text{ L}}} \approx 16 \text{ hrs}$$

↑                          ↑                          ↑  
 Oxidant addition rate    Concentr. added oxidant    Total vol. solution  
 [Page 4]                [Page 4]                [Methods]

In the Nat. Chem. paper [oscillations]:

$$\tau \approx \frac{0.058 \text{ mmol}}{45 \frac{\mu\text{L}}{\text{hr}} \cdot 1.12 \text{ M} \cdot \frac{1}{4 \text{ mL}}} = \frac{5.8 \cdot 10^{-3} \text{ mmol}}{4.5 \cdot 10^{-5} \frac{\text{L}}{\text{hr}} \cdot 1.12 \frac{\text{mol}}{\text{L}}} \approx 1 \text{ hr}$$

We then have dimensionless parameters:

$$\lambda = \frac{\tilde{C}_{Auc}}{\tilde{C}_{A_2}} \quad \left\{ \begin{array}{l} \text{Nat. Comm. } \lambda \approx \frac{0.2 \text{ mM}}{20 \text{ mM}} \approx 10^{-2} \\ \text{Nat. Chem. } \lambda \approx \frac{[0.52, 1.56]}{0.058 \text{ mmol}} \approx [3.5 \cdot 10^{-2}, 10^{-1}] \end{array} \right.$$

$$\epsilon = \frac{r_{ext}}{k_0 \tilde{C}_{A_2}^3} \ll 1 \quad [\text{hopefully}]$$

$$\delta = \frac{r_{ext}}{k_{dm} \tilde{C}_{A_2}} \ll 1 \quad [\text{hopefully}]$$

$$\alpha = \frac{k_s^* \tilde{C}_{Auc} \tilde{C}_{A_2}}{n r_{ext}}$$

$$\Theta = \frac{k_s \tilde{C}_{A_2}}{r_{ext}}$$

$$\beta = \frac{k_{ds}^* \tilde{C}_{Auc} \tilde{C}_{A_2}}{n r_{ext}}$$

$$\phi = \frac{k_{ds} \tilde{C}_{A_2}}{r_{ext}}$$

No idea how large or small a priori

$$K = \frac{k_{ds}}{k_0 \tilde{C}_{A_2}^2}$$

So the final nondimensional equations are:

$$\frac{dc_A}{dt} = C_0 \left[ 2(1 - c_{A_2}) - \lambda(c_S + c_M) \right]^2 - \alpha c_M c_{A_2} - \delta c_{A_2}$$

$$\frac{dc_S}{dt} = \frac{\alpha}{\lambda} c_M c_{A_2} - \beta c_M c_S + \frac{\theta}{\lambda} c_{A_2} - \phi c_S - \frac{1}{\delta} [c_S^m - c_M]$$

$$\frac{dc_0}{dt} = \frac{1}{\varepsilon} \left\{ 1 - C_0 \left[ 2(1 - c_{A_2}) - \lambda(c_S + c_M) \right]^2 - K C_0 \right\}$$

$$\frac{dc_M}{dt} = \frac{1}{\delta} [c_S^m - c_M]$$

## FINAL (DIMENSIONLESS) FORM OF THE MODEL

With initial conditions:

$$c_{A_2}(t=0) = 1$$

$$c_S(t=0) = 0$$

$$c_0(t=0) = 0$$

$$c_M(t=0) = 0$$

And where the thiolate concentration is:

$$c_A = 2(1 - c_{A_2}) - \lambda(c_S + c_M)$$

### ASYMPTOTIC MODEL 1

$$\delta, \varepsilon, K = 0 \Rightarrow \begin{cases} c_M = c_S^m \\ c_0 = \frac{1}{[2(1 - c_{A_2}) + \lambda(c_S + c_M)]^2} \end{cases}$$

$$\frac{dc_{A_2}}{dt} = 1 - \alpha c_{A_2} c_S^m - \delta c_{A_2}$$

$$\frac{dc_S}{dt} = \frac{\alpha}{\lambda} c_{A_2} c_S^m - \beta c_S^{m+1} + \frac{\theta}{\lambda} c_{A_2} - \phi c_S$$

$$c_{A_2}(0) = 1$$

$$c_S(0) = 0$$