Supplementary Information

# Homogeneous Organic Crystal Nucleation Rates in Solution from the Perspective of Chemical Reaction Kinetics

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## SI1 - Size distribution of reversible aggregates – full derivation

Mass balance of the overall activity of an ideal solution and the activities of the reversible aggregates $M_n$

$$\mathrm{a}_0 = \sum_{n=1}^{\infty} n\mathrm{a}_\mathrm{n}$$

With K =1 (reversible aggregation), it follows that (see main text)

$$\mathrm{a}_\mathrm{n} = a_1^n$$

And therefore

$$\mathrm{a}_0 = \sum_{n=1}^{\infty} n a_1^n$$

The term on the right hand side is a standard power series with the solution

$$\sum_{n=1}^{k} n a_1^n = \mathrm{a}_1 \frac{1-(k+1)a_1^k + k a_1^{k+1}}{(1-\mathrm{a}_1)^2}$$

For $k \to \infty$,

$$a_1^k = 0$$

$$a_1^{k+1} = 0$$

Hence

$$\mathrm{a}_0 = \sum_{n=1}^{\infty} n a_1^n = \frac{\mathrm{a}_1}{(1-\mathrm{a}_1)^2}$$

Solve for $\mathrm{a}_1$

$$\mathrm{a}_0(1-\mathrm{a}_1)^2 = \mathrm{a}_1$$

$$a_1^2 - \left(2+\frac{1}{\mathrm{a}_0}\right)\mathrm{a}_1 + 1 = 0$$

This is a second order polynomial of the form $jx^2 + kx + l$ with

$$j = 1;\ k = -\left(2+\frac{1}{\mathrm{a}_0}\right);\ l = 1$$

Solve with quadratic formula

$$\mathrm{a}_1 = \frac{-k \pm \sqrt{k^2-4jl}}{2j} = \frac{\left(2+\frac{1}{\mathrm{a}_0}\right) \pm \sqrt{\left(2+\frac{1}{\mathrm{a}_0}\right)^2 - 4}}{2} = \left(1+\frac{1}{2\mathrm{a}_0}\right) \pm \frac{1}{2\mathrm{a}_0}\sqrt{4\mathrm{a}_0+1}$$

Only the subtraction gives a meaningful solution; now introduce $1+\sqrt{4\mathrm{a}_0+1}$ in the denominator,

$$\mathrm{a}_1 = \frac{\left(\left(1+\frac{1}{2\mathrm{a}_0}\right) - \frac{1}{2\mathrm{a}_0}\sqrt{4\mathrm{a}_0+1}\right)\left(1+\sqrt{4\mathrm{a}_0+1}\right)}{1+\sqrt{4\mathrm{a}_0+1}}$$

Algebra simplifies the numerator to

$$\mathrm{a}_1 = \frac{\sqrt{4\mathrm{a}_0+1}-1}{\sqrt{4\mathrm{a}_0+1}+1} = \frac{m-1}{m+1}$$

with

$$m = \sqrt{4\mathrm{a}_0+1}$$

Final expression for the aggregate size distribution, using $\mathrm{a_n} = a_1^n$ from above:

$$\mathrm{a_n} = \left(\frac{\sqrt{4a_0+1}-1}{\sqrt{4a_0+1}+1}\right)^n = \left(\frac{\mathrm{m}-1}{\mathrm{m}+1}\right)^n$$

Since this is an ideal solution we can replace the activities by the concentrations $[M_n]$ and $[M]_0$ according to

$$a_0 = \frac{[M]_0}{c^{\ominus}}$$

With

$$c^{\ominus} = 1\ \frac{\mathrm{mol}}{\mathrm{dm}^3}$$

Giving

$$[\mathrm{M_n}] = c^{\ominus}\left(\frac{\sqrt{4[\mathrm{M}]_0/c^{\ominus}+1}-1}{\sqrt{4[\mathrm{M}]_0/c^{\ominus}+1}+1}\right)^n$$

Numerically, since $c^{\ominus} = 1\ \frac{\mathrm{mol}}{\mathrm{dm}^3}$, the concentration $[\mathrm{M_n}]$ of any aggregate with n solute molecules in mol $\mathrm{dm}^{-3}$ is thus given by

$$[\mathrm{M_n}] = \left(\frac{\sqrt{4[\mathrm{M}]_0+1}-1}{\sqrt{4[\mathrm{M}]_0+1}+1}\right)^n$$

## SI2 - Calculation of n*

$$[\mathrm{M_n}] = \left(\frac{\mathrm{m}-1}{\mathrm{m}+1}\right)^{n}$$

with

$$m = \sqrt{4[M]_0 + 1}$$

Condition for solubility $[\mathrm{M}]_0^*$: number of aggregates with n* must be at least 1.

$$\mathrm{N_{n^*}} = [\mathrm{M_{n^*}}]N_A V = 1$$

Combine the above equations with $[M]_0 = [\mathrm{M}]_0^*$

$$\left(\frac{\sqrt{4[\mathrm{M}]_0^* + 1} - 1}{\sqrt{4[\mathrm{M}]_0^* + 1} + 1}\right)^{\mathrm{n}^*} N_A V = 1$$

Solve

$$\left(\frac{\sqrt{4[\mathrm{M}]_0^* + 1} - 1}{\sqrt{4[\mathrm{M}]_0^* + 1} + 1}\right)^{\mathrm{n}^*} = \frac{1}{N_A V}$$

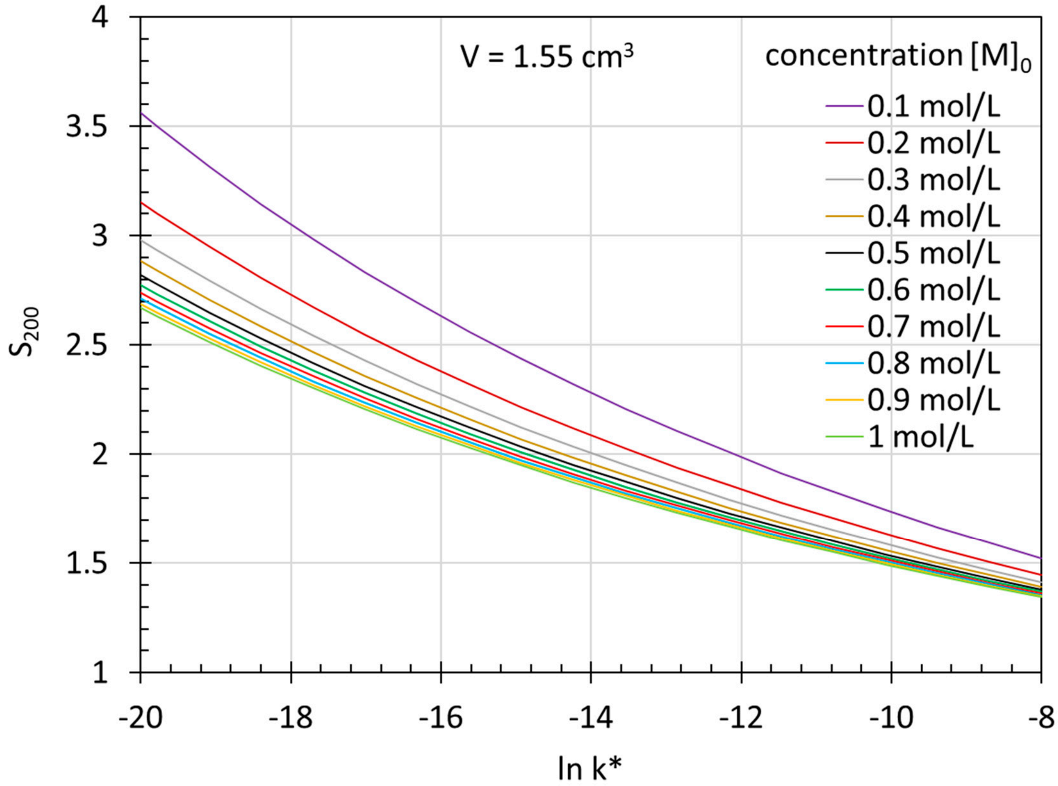
$$\mathrm{n}^* \ln\left(\frac{\sqrt{4[\mathrm{M}]_0^* + 1} - 1}{\sqrt{4[\mathrm{M}]_0^* + 1} + 1}\right) = -\ln(N_A V)$$

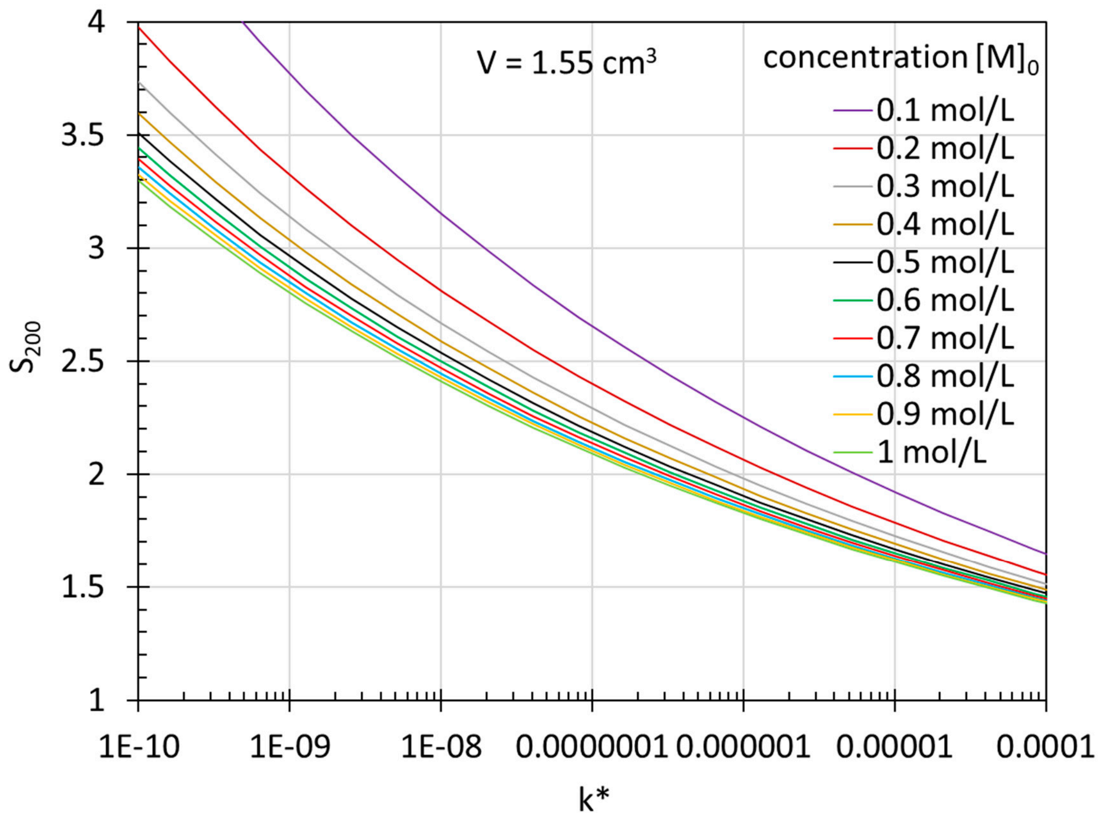
$$\mathrm{n}^* = -\frac{\ln(N_A V)}{\ln\left(\frac{\sqrt{4[\mathrm{M}]_0^* + 1} - 1}{\sqrt{4[\mathrm{M}]_0^* + 1} + 1}\right)}$$

The resulting value for n* should be rounded down to the nearest integer.

**SI3 - Dependence of $S_{200}$ on k* and ln(k*) as a function concentration**

Calculated for a solution volume of 1.55 $cm^3$



**SI4 – Fits to experimental data for the 10 benzoic acid systems as a function of supersaturation S**