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C₆₀ FULLERENE AGGREGATION IN AQUEOUS SOLUTION

by

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Derivation of the equations for the strict model of C₆₀ fullerene aggregation

As long as the surface of a micelle comprising i -molecules contains a large number, N_i , of potential binding sites for single fullerene molecules, in order to obtain the correct magnitude for the microscopic binding constant, K_F , it is necessary to take into consideration the distribution of bound C₆₀ molecules over all available binding sites on the cluster. It is also necessary to consider that within the framework of the physical model used, the growth of clusters is assumed upon increased fullerene concentration. Hence, each bound fullerene molecule increases the dimension of a cluster and thereby increases the number of sites available for binding for the next fullerene molecule.

Let us take the estimated value of N_i to be the number of square sections of one C₆₀ molecule (i.e. d_1^2), which can be placed on the surface of a cluster with diameter d_i

$$N_i = \left[\pi \left(\frac{d_i}{d_1} \right)^2 \right] = \left[\pi \cdot i^{2/3} \right], \quad (\text{S1})$$

where the square brackets stand for the integer part of the number. Hence, the total number of possibilities of binding $(i - M)$ molecules with the nucleus of a cluster equals $\frac{1}{(i - M)!} \prod_{j=M}^{i-1} N_j$, which allows the expression to be written for the mole fraction of clusters containing the given number i of fullerene molecules in it ($i > M$):

$$f_i = \frac{C_{M0}}{r} \frac{(K_F C_1)^{i-M}}{(i - M)!} \prod_{j=M}^{i-1} N_j. \quad (\text{S2})$$

Equation S2, when substituted into eq 4, gives a complete description of the experimental curve $d_z(C_0/r)$. Besides this, eq S2 allows the mass balance equation to be written thus:

$$\frac{C_0}{r} = C_1 + M \frac{C_{M0}}{r} + \sum_{i=M+1}^{\infty} i f_i. \quad (\text{S3})$$

Solution of S3 at each experimental point enables the monomer concentration C_1 to be found. It follows that fitting of the experimental data in Figure 2 by means of the theoretical curve (eq 4) is accomplished using four adjustable parameters: C_{M0} , A , K_F , M .

Unfortunately the sums and the products in eqs S2 and S3 cannot be transformed into closed analytical forms and must be evaluated numerically. Fitting of the dependence $d_z(C_0/r)$ in Figure 2 using model eq 4 and eq S3 appears to be impossible because the summation and product operations need to be accomplished in these equations per molecule and therefore the range of indexes run cover the range of the same order of magnitude as the number M , i.e. 10^6 . Removal of this difficulty is potentially possible if the sums are evaluated analytically. The latter, in its turn, is possible by introducing further approximations into the model and by considering a macroscopic

binding constant, K'_F , which does not take into consideration the distribution of bound monomers on the surface of a cluster.

If K'_F is given as a macroscopic constant, the eq S2 may be re-written in a simpler form thus:

$$f_i = \frac{C_{M0}}{r} (K_F C_1)^{i-M}. \quad (\text{S4})$$

Substituting eq S4 into eq S3 gives

$$\frac{C_0}{r} = C_1 + M \frac{C_{M0}}{r} + \sum_{i=M+1}^{\infty} i \frac{C_{M0}}{r} (K_F C_1)^{i-M}$$

or

$$C_0 = rC_1 + C_{M0} \sum_{i=M}^{\infty} i (K_F C_1)^{i-M}.$$

The last equation is further transformed taking account of the fact that $M \ll 1$:

$$\begin{aligned} C_0 &= rC_1 + C_{M0} \sum_{i=0}^{\infty} (i+M) (K_F C_1)^i = rC_1 + C_{M0} \sum_{i=0}^{\infty} i (K_F C_1)^i + MC_{M0} \sum_{i=0}^{\infty} (K_F C_1)^i \\ C_0 &= rC_1 + C_{M0} \frac{M - (M-1)K_F C_1}{(1 - K_F C_1)^2} \approx rC_1 + \frac{MC_{M0}}{1 - K_F C_1}. \end{aligned} \quad (\text{S5})$$

Equation S5 represents the mass balance equation. Further simplification is possible if the index i does not reach the values close to M . Under such an assumption it is possible to find the exact concentration of monomeric fullerenes:

$$C_1 = \frac{r + K_F C_0 - \sqrt{(r - K_F C_0)^2 + 4rK_F MC_{M0}}}{2rK_F}. \quad (\text{S6})$$

Evaluation of eq 4 taking account of eq S4 gives:

$$d_z = \frac{d_1}{1 + A \frac{C_{M0}}{r}} \cdot \frac{\sum_{i=M}^{\infty} i^2 f_i}{\sum_{i=M}^{\infty} i^{5/3} f_i} = \frac{rd_1}{r + AC_{M0}} \cdot \frac{\sum_{i=0}^{\infty} (i+M)^2 (K_F C_1)^i}{\sum_{i=0}^{\infty} (i+M)^{5/3} (K_F C_1)^i}.$$

The sum in the denominator cannot be analytically transformed, whereas the sum in the numerator is evaluated as the following:

$$\begin{aligned} \sum_{i=0}^{\infty} (i+M)^2 (K_F C_1)^i &= \sum_{i=0}^{\infty} i^2 (K_F C_1)^i + 2M \sum_{i=0}^{\infty} i (K_F C_1)^i + M^2 \sum_{i=0}^{\infty} (K_F C_1)^i = \\ &= \frac{(1 + K_F C_1) K_F C_1}{(1 - K_F C_1)^3} + \frac{2MK_F C_1}{(1 - K_F C_1)^2} + \frac{M^2}{1 - K_F C_1} = \\ &= \frac{(M^2 - (M-1)^2 K_F C_1)(1 - K_F C_1) + 2K_F C_1}{(1 - K_F C_1)^3}. \end{aligned}$$

Finally one gets:

$$d_z = \frac{rd_1}{r + AC_{M0}} \left(\frac{M^2 - (M-1)^2 K_F C_1}{(1 - K_F C_1)^2} + \frac{2K_F C_1}{(1 - K_F C_1)^3} \right) \frac{1}{\sum_{i=0}^{\infty} (i+M)^{5/3} (K_F C_1)^i}. \quad (\text{S7})$$

Equations S6 and S7 are the key equations of the strict model with a macroscopic binding constant. Unfortunately, in this case the fitting of data has also appeared impossible due to the presence of the analytically unconvertible infinite sum in the denominator of eq S7, where the range of the indexes' run has an order of 10^6 .