Comments on the Interpretation of Triplet Excited-state Decay Data for the Determination of the Equilibrium Constants in Host–Guest Cyclodextrin Complexes

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The mathematical analysis reported by van Stam et al. in the preceding communication is shown to lead to the same quantitative results as previously published.

In the preceding communication van Stam et al.[1] presented a mathematical treatment from which they concluded that our treatment led to incorrect values for the rate constants of triplet xanthone complexation with cyclodextrins (CDs).[2] In addition, they suggested that the rate constants in question could only be recovered by a global analysis of the kinetic data.

Global analysis has been developed to obtain kinetic information from complex systems. In an early publication on the subject, global analysis[3] and a previously employed simpler method based on the same equations[4] were compared. The absolute values for the rate constants recovered by both methods were the same, but the errors for the global analysis treatment were much smaller. This shows that global analysis is not a requirement to obtain quantitative data, but that it has distinct benefits regarding the quality of the data. It is important to note that the mechanistic scheme in this comparison is the same as that for triplet xanthone complexation with CDs.

The second claim by van Stam et al.[1] was that our analysis of the data led to incorrect values for the rate constants. The mathematical treatment we employed can be derived from the treatment presented by van Stam et al.[1] The time evolution for free and bound xanthone is given by eqns. (5) and (6), and the pre-exponential factors are given in eqns. (8a)–(8d) in the preceding communication.[1] The exponential factors $\gamma_{1,2}$ [eqn. (10) in ref. 1] are given by eqn. (A)

$$\gamma_{1,2} = -\frac{1}{2}\left[\frac{(k_+[CD] + k_{x(aq)} + k_-) \pm}{\sqrt{(k_+[CD] + k_{x(aq)} - k_-)^2 + 4k_- k_+[CD]}}\right] \quad (A)$$

The transient absorption (ΔA) at any given wavelength is given by eqn. (B)

$$\Delta A = \varepsilon_{x(aq)} \, l[X(aq)^*]_t + \varepsilon_{x(CD)} \, l \, [X(CD)^*]_t \quad (B)$$

Substituting eqns. (5) and (6) of the previous communication and the relationship that $\beta_{21} = -\beta_{11}$ into eqn. (B) gives eqn. (C).

$$\Delta A = (\varepsilon_{x(aq)} - \varepsilon_{x(CD)}) \, l \, \beta_{11} \exp(\gamma_1 \, t) + (\varepsilon_{x(aq)}\beta_{12} + \varepsilon_{x(CD)}\beta_{22}) \, l \exp(\gamma_2 \, t) \quad (C)$$

The values for γ_1 and γ_2 are recovered from the experimental data, and the sum of the exponential factors is derived from eqn. (A) as eqn. (D).

$$\gamma_1 + \gamma_2 = -(k_+ [CD] + k_{x(aq)} + k_-) \quad (D)$$

Assuming that $\gamma_1 \gg \gamma_2$ and $k_{x(aq)} \ll (k_+[CD] + k_-)$, which is justified in our system, the fast rate constant is given by eqn. (E).

$$\gamma_1 = -(k_+[CD] + k_-) \quad (E)$$

Equation (E) corresponds to that employed in our previous analysis.[2] If the same assumptions are introduced at an earlier stage of the argument eqns. (9a) and (9b) of van Stam et al.[1] are obtained. In the case of xanthone CD complexes, the values for γ_1 and γ_2 have to be obtained from kinetic traces collected at different time domains, since their values are quite different. However, γ_1 cannot be obtained by fitting the data to a single exponential plus a constant value, since ΔA never levels off. In the original set of data γ_2 was estimated from the fit of the decay

at longer times to a single exponential decay. In order to compare the values of k_- and k_+ recovered from eqns. (D) and (E) we refitted out data for β- and Hp-β-CD. The γ_2 values were obtained by fitting the data at long time bases to the sum of two exponentials,† and the recovered γ_2 values were kept constant when γ_1 was recovered from the fit to two exponentials of the decay at short times. Fig. 1 shows a comparison for the data fitted to eqns. (D) after van Stam et al. and (E). The values for ($\gamma_1 + \gamma_2$) are slightly higher than for γ_1. However, the difference was negligible when compared to the experimental uncertainties in our data, showing that there is no advantage in using eqn. (D) over eqn. (E). The values obtained from eqn. (5) for the refitted data are compared to the original data in Table 1. For all cases, except the association rate constant of triplet xanthone with β-CD, the values are within the experimental uncertainties quoted initially. The value for k_+ and β-CD is lower than previously obtained, because of a different fit (not
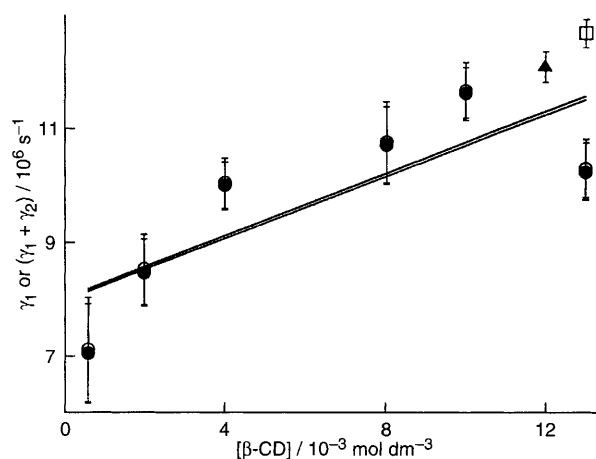

Fig. 1 Dependence of γ_1 (●) and ($\gamma_1 + \gamma_2$) (○) recovered from the fitting of the triplet xanthone decay (620 nm) at different β-CD concentrations for one experiment. The lower line corresponds to the fitting of the γ_1 values to eqn. (E), and the upper line corresponds to the fitting of the ($\gamma_1 + \gamma_2$) values to eqn. (D). (□) and (▲) correspond to γ_1 values from independent experiments.

Table 1 Dissociation and association rate constants and equilibrium constants of triplet xanthone with β-cyclodextrins previously published[2] and after re-fitting the data[a]

	β-CD		Hp-β-CD	
	previous data	refitted data	previous data	refitted data
$k_+/10^8$ dm³ mol⁻¹ s⁻¹	4 ± 1	2 ± 1	1.4 ± 0.3	1.0 ± 0.4
$k_-/10^6$ s⁻¹	8.4 ± 0.7	9.1 ± 0.7	7.1 ± 0.4	7.1 ± 0.7
$K_T/$dm³ mol⁻¹	48 ± 13	22 ± 11	20 ± 4	14 ± 6

[a] The uncertainties are standard deviations from pooled data.

different analysis). This result is not unreasonable taking into account the uncertainties involved.†

We want to emphasize that the objective of our work was to show the usefulness of employing triplet xanthone to probe the dynamics of excited state complexation and to compare its behaviour with that of the ground state. Thus, our previous conclusions and quantifications, taking into account the uncertainties stated, are correct. This proves that use of simple equations derived for complex systems by making valid approximations is a useful and time saving approach.

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† A variation in the baseline is frequently observed, even after correction shots were accumulated, due to irreproducible pulses from the Xe-arc lamp employed for the absorbance measurements. To avoid biases, the γ_2 values were obtained by fitting the data with the baseline at zero and at any offset. The γ_2 values obtained for different baselines were averaged.

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