Comments Concerning "The Effect of Temperature on the Fluorescence Quenching of Perylene by Tetrachloromethane in Mixtures with Cyclohexane and Benzene"

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An indirect spectrofluorometric probe method is developed for calculating equilibrium constants for formation of heterogeneous solvent-solvent molecular complexes from measured fluorescence emission intensities in select systems that exhibit parabolic-shaped Stern-Volmer quenching plots.

In a recent paper, Wiczk and Latowski [1] examined the effect of temperature on the fluorescence quenching of perylene by tetrachloromethane in mixtures with cyclohexane and benzene. The authors observed an unusual "parabolic-shaped" curve in the case of the binary tetrachloromethane + benzene system when plotting the ratio of fluorescent quantum yields, ϕ_0/ϕ, versus the stoichiometric molarity of tetrachloromethane, $[CCl_4]_{total}$. The quantities ϕ_0 and ϕ refer to measured quantum yields in the absence and in the presence of tetrachloromethane, respectively. Alternatively the authors could have plotted the ratio of experimental fluorescence intensities, F_0/F, versus $[CCl_4]_{total}$. Observed non-linearity and the parabolic shape in the ϕ_0/ϕ versus $[CCl_4]_{total}$ Stern-Volmer plot was rationalized in terms of two quenchers being present in solution, the free *uncomplexed* CCl_4 and a persumed $C_6H_6-CCl_4$ molecular complex. The complex was assumed to be more effective in quenching the fluorescence emission of perylene.

The purpose of the present communication is not to criticize the excellent work of Wiczk and Latowski. Rather, I wish to show how their ideas, when combined with a reasonable thermodynamic solution model and simplifying approximations, can lead to the development of an experimental method for determining equilibrium constants of presumed heterogeneous solvent-solvent molecular complexes based upon measured fluorescence emission intensities. For simplicity, I will assume that the *uncomplexed* CCl_4 molecules and the $C_6H_6-CCl_4$ complex both act as dynamic quenchers:

$$\begin{aligned} &\text{Perylene} + h\nu && \rightarrow \text{Perylene}^*, \\ &\text{Perylene}^* + CCl_4 && \rightarrow \text{Perylene} + CCl_4, \\ &\text{Perylene}^* + C_6H_6-CCl_4 && \rightarrow \text{Perylene} + C_6H_6-CCl_4, \end{aligned}$$

where k_{CCl_4} and $k_{C_6H_6-CCl_4}$ denote the two quenching rate constants. The ratio of the fluorescent quantum yields, ϕ_0/ϕ, is given by [2, 3]

$$\begin{aligned} (\phi_0/\phi) - 1 &= (F_0/F) - 1 \\ &= k_{CCl_4}[CCl_4]_{free} + k_{C_6H_6-CCl_4}[C_6H_6-CCl_4] \end{aligned} \tag{1}$$

or by

$$\begin{aligned} &[(\phi_0/\phi) - 1]\,(X^0_{CCl_4} V_{CCl_4} + X^0_{C_6H_6} V_{C_6H_6}) \\ &\quad = [(F_0/F) - 1]\,(X^0_{CCl_4} V_{CCl_4} + X^0_{C_6H_6} V_{C_6H_6}) \\ &\quad = k_{CCl_4}\, r_{CCl_4,\,free} + k_{C_6H_6-CCl_4}\, r_{comp}\,, \end{aligned} \tag{2}$$

where

$$\begin{aligned} r_{CCl_4,\,free} = &\text{ moles of free } CCl_4/ \\ &(\text{moles of } CCl_4 + \text{moles of } C_6H_6)\,, \end{aligned} \tag{3}$$

$$\begin{aligned} r_{comp} = &\text{ moles of } C_6H_6-CCl_4/ \\ &(\text{moles of } CCl_4 + \text{moles of } C_6H_6)\,, \end{aligned} \tag{4}$$

if one converts the molarities to mole numbers by multiplying by the molar volume of the solution, $V_{solution} = X^0_{CCl_4} V_{CCl_4} + X^0_{C_6H_6} V_{C_6H_6}$. The fluorophore is at ca. 10^{-5} Molar (or less) and its presence has a negligible contribution on the solution volume. Mole fractions are denoted as X_i, and the superscript $(^0)$ indicates the original stoichiometric binary solvent compositions, calculated as if the molecular complex were not present. Also, it is assumed that the molar volume of the $C_6H_6-CCl_4$ molecular complex equals the sum of the molar volumes of benzene and tetrachloromethane, and that ΔV of mixing equals zero. Equations (1) and (2) also apply if both CCl_4 and $C_6H_6-CCl_4$ act as static quenching agents; however, in this latter case the two rate constants would be replaced by equilibrium constants for the formation of nonfluorescent ground state perylene–CCl_4 and perylene–$C_6H_6-CCl_4$ complexes. The mathematical treatment of fluorescence quenching in the case of a combined static-dynamic quenching mechanism is discussed elsewhere [4–6] and will not be considered in the present communication.

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Formation of the presumed benzene-tetrachloromethane molecular complex is described by

$$C_6H_6 + CCl_4 \rightleftharpoons C_6H_6\text{–}CCl_4\,, \qquad (5)$$

$$K_{eq} = X_{C_6H_6-CCl_4}/(X^{free}_{C_6H_6}\,X^{free}_{CCl_4})\,,$$

with the corresponding equilibrium constant being expressed in mole fraction concentration units, which would be consistent with the Ideal Associated Solution (IAS) thermodynamic model [7–13] and Raoult's law definition of solution ideality. Stoichiometric mole fractions of benzene and tetrachloromethane must sum to unity, $X^0_{CCl_4} + X^0_{C_6H_6} = 1$, and are related to the mole fractions of the *uncomplexed*, free CCl_4 and free C_6H_6 via

$$X^{free}_{CCl_4} = (X^0_{CCl_4} - r_{comp})/(1 - r_{comp})\,, \qquad (6)$$

$$X^{free}_{C_6H_6} = (X^0_{C_6H_6} - r_{comp})/(1 - r_{comp})\,, \qquad (7)$$

$$X_{C_6H_6-CCl_4} = r_{comp}/(1 - r_{comp})\,, \qquad (8)$$

simple mass balance constraints.

Equations (5)–(8) are combined to give the expression for the C_6H_6–CCl_4 association constant

$$K_{eq} = r_{comp}\,(1 - r_{comp})/[(X^0_{CCl_4} - r_{comp})\,(X^0_{C_6H_6} - r_{comp})]\,, \qquad (9)$$

which after suitable mathematical manipulations is rearranged to

$$K_{eq}\,X^0_{CCl_4}\,X^0_{C_6H_6} - K_{eq}\,r_{comp} + K_{eq}\,r^2_{comp} = r_{comp} - r^2_{comp}\,, \qquad (10)$$

$$X^0_{CCl_4}\,X^0_{C_6H_6}/r_{comp} = -[(K_{eq}+1)/K_{eq}]\,r_{comp} + (K_{eq}+1)/K_{eq}\,, \qquad (11)$$

Similarly, (2) is rewritten as

$$[(F_0/F) - 1]\,(X^0_{CCl_4}\,V_{CCl_4} + X^0_{C_6H_6}\,V_{C_6H_6}) = k_{CCl_4}\,X^0_{CCl_4} + r_{comp}\,[k_{C_6H_6-CCl_4} - k_{CCl_4}]\,, \qquad (12)$$

$$r_{comp}\,[k_{C_6H_6-CCl_4} - k_{CCl_4}] = [(F_0/F) - 1]\,(X^0_{CCl_4}\,V_{CCl_4} + X^0_{C_6H_6}\,V_{C_6H_6}) - k_{CCl_4}\,X^0_{CCl_4}. \qquad (13)$$

Every term on the right-hand side of (13) is known, either from direct experimental fluorescence measurements (F and F_0), or known from the initial binary solvent compositions ($X^0_{CCl_4}$ and $X^0_{C_6H_6}$), or known from properties of the pure components (V_{CCl_4} and $V_{C_6H_6}$). The quenching rate constant k_{CCl_4} is calculated from (12) as $k_{CCl_4} = [(F_0/F_{CCl_4}) - 1]\,V_{CCl_4}$, using the fluorescence emission intensity of perylene measured in pure tetrachloromethane, F_{CCl_4}. For notational simplicity, the entire right-hand side of (13) is denoted as Y, giving $r_{comp}\,[k_{C_6H_6-CCl_4} - k_{CCl_4}] = Y$.

Substituting $r_{comp} = Y/[k_{C_6H_6-CCl_4} - k_{CCl_4}]$ into (11), the following expression is derived:

$$(X^0_{CCl_4}\,X^0_{C_6H_6})/Y = -\{[K_{eq}+1)/K_{eq}]/[k_{C_6H_6-CCl_4} - k_{CCl_4}]^2\}\,Y + [(K_{eq}+1)/K_{eq}]/[k_{C_6H_6-CCl_4} - k_{CCl_4}]\,. \qquad (14)$$

Careful examination of (14) reveals that a plot of $X^0_{CCl_4}\,X^0_{C_6H_6}/Y$ versus Y should be linear, with slope $= -[(K_{eq}+1)/K_{eq}]/[k_{C_6H_6-CCl_4} - k_{CCl_4}]^2$ and intercept $= [(K_{eq}+1)/K_{eq}]/[k_{C_6H_6-CCl_4} - k_{CCl_4}]$. Numerical values of the perylene–C_6H_6–CCl_4 quenching constant, $k_{C_6H_6-CCl_4}$, and the equilibrium constant for complex formation, K_{eq}, can be determined from the least-squares slope and intercept as $k_{C_6H_6-CCl_4} - k_{CCl_4} = -$(intercept/slope) and as $(K_{eq}+1)/K_{eq} = -[(\text{intercept})^2/\text{slope}]$. The preceding discussion clearly shows that in certain instances spectrofluorometric probe quenching measurements can provide a convenient, independent experimental method for studying heterogeneous solvent-solvent molecular complexes in fluid solution.

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