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THE UNRELIABILITY OF ASSOCIATION CONSTANTS OF ORGANIC CHARGE-TRANSFER COMPLEXES DERIVED FROM OPTICAL ABSORPTION SPECTRA—I

GENERAL CONSIDERATIONS

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Abstract—It is suggested that certain anomalies which arise from the evaluation of equilibrium constants of organic charge-transfer complexes are the result of deviations from Beer's law of the optical absorption characteristic of the complexes.

MANY algebraic methods have been used to evaluate the association constants (K) and extinction coefficients (ϵ) of organic charge-transfer complexes from a series of solutions containing an electron donor, D, and an electron acceptor, A, for example.[1-8] Most of these are variants or modifications of the method described by Benesi and Hildebrand.[9] With very few exceptions, solutions containing a large excess of one or other of the component molecular species are used. It is generally considered that a 1:1 complex (AD) is formed:

$$A + D \rightleftharpoons AD \qquad (1)$$

So that the equilibrium may be represented by a simple mass-action constant* K_c where:

$$K_c = [AD]/[A][D] \text{ l.mole}^{-1} \qquad (2)$$

where [AD], [A] and [D] are the concentrations of these species expressed in moles.l^{-1}. All optical methods assume that the complex has an optical absorption, which if it could be separated from the absorptions of the other species present, would be proportional to the optical density, i.e. obey Beer's Law. In the case of complex formation where contact charge-transfer (see below) is postulated as well[10] the explicit assumption is still made that the molecular complex itself obeys Beer's law. The association constants and extinction coefficients evaluated from such analyses have

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* Sometimes an alternative dimensionless association constant K_x has been used, where $K_x = [AD]/[A](D)$ and (D) = mole fraction of D. For ideal dilute solutions, $K_x = K_c\,.\,(1000d/M)$ where d = density and M = mol. wt. of the solvent.

[1] L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.* 73, 4169 (1951).

[2] J. A. A. Keltelaar, C. van de Stolpe, A. Goudsmit and W. Dzcubas, *Rec. Trav. Chim.* 71, 1104 (1952).

[3] R. Foster, D. Ll. Hammick and A. A. Wardley, *J. Chem. Soc.* 3817 (1953).

[4] R. L. Scott, *Rec. Trav. Chim.* 75, 787 (1956).

[5] P. A. D. de Maine, *J. Chem. Phys.* 26, 1042 (1957).

[6] N. J. Rose and R. S. Drago, *J. Amer. Chem. Soc.* 81, 6138 (1959).

[7] C. P. Nash, *J. Phys. Chem.* 64, 950 (1960).

[8] G. Cilento and D. L. Sanioto, *Z. Physik. Chem.* 223, 333 (1963).

[9] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.* 71, 2703 (1949).

[10] L. E. Orgel and R. S. Mulliken, *J. Amer. Chem. Soc.* 79, 4839 (1957).

given rise to several anomalies. Probably the most discussed is the relationship between K and ϵ for a set of complexes, for example of a series of donors with a given acceptor. It has been pointed out[10,11] that in such a series, as the electron donor becomes more effective and K increases, the transition moment should increase, and an increase in ϵ would be expected. Numerous examples of the converse have been noted. Mulliken and Orgel[10] endeavoured to explain the observed results by postulating that the absorption extra to the component molecules is not only the result of complex (DA) pairs, but that there is also a contribution from collision complexes (contact charge-transfer). Later Murrell[11] suggested that such results could be explained in terms of energy borrowing by the charge-transfer transition from levels in one of the component molecules.

More recently Murrell *et al.*[12] have suggested that the free donor, free acceptor and complex occur in solution with well defined solvent shells, that the equilibrium governing complex formation is not (1) but:

$$\mathrm{ASn} + \mathrm{DSm} \rightleftharpoons \mathrm{(AD)Sp} + \mathrm{qS} \tag{3}$$

where n, m and p are the number of solvent molecules (S) associated with the species A, D and AD respectively and $n + m = p + q$, whence it may be shown that:

$$K_{\mathrm{exp}} = K_{\mathrm{true}} - \frac{q(m + 1)}{S_0} \tag{4}$$

and

$$\epsilon_{\mathrm{exp}} = \epsilon_{\mathrm{true}} \cdot \left(\frac{K_{\mathrm{true}}}{K_{\mathrm{exp}}}\right) \tag{5}$$

where K_{exp}, ϵ_{exp} are the experimentally determined values of K_c and ϵ using the Benesi–Hildebrand or similar evaluation, K_{true} is the equivalent constant for reaction (3) and S_0 is the total solvent concentration when $[D] = 0$. They suggest that the term $q(m + 1)/S_0$ may often have a value 1–3 $\mathrm{l.mol^{-1}}$, so that K's of the order 10 $\mathrm{l.mol^{-1}}$ may be in some error and many association constants with apparent values $\sim$1–2 $\mathrm{l.mol^{-1}}$ may be in error by 100% or more. There will be a corresponding error in ϵ, as is shown by Eq. 5. Evidence against this theory is the constancy observed in the value of ϵ obtained by Benesi–Hildebrand type evaluations for a given complex in a series of solvents, (Table 1). If for such complexes the term $q(m + 1)/S_0$ in Eq. 4 is significant, then its importance should increase as K decreases, both relatively and in actual magnitude since K is smaller in solvents of greater solvating power. By Eq. 5 this should be reflected in an increase in ϵ_{exp} as K_{exp} decreases. Such is not the case in systems where the data are available (Table 1).

Another anomaly, rarely admitted, is the difference in values of K_c and ϵ for a given system obtained by different groups of workers.[13] Virtually all determinations use the condition $[D] \gg [A]$ mainly because of the low solubility of many electron acceptors in most solvents used. Although in some cases where the condition $[D] \ll [A]$ has been used consistent values have been obtained,[3] in other cases such experimental conditions give rise to very large differences in K_c and ϵ compared with the results

[11] J. N. Murrell, *J. Amer. Chem. Soc.* **81**, 5037 (1959); *Quart. Rev.* **15**, 191 (1961).

[12] S. Carter, J. N. Murrell and E. J. Rosch, *J. Chem. Soc.* 2048 (1965).

[13] e.g. R. Foster, *J. Chem. Soc.* 1075 (1960).

where [D] $\gg$ [A]. One such example is the system N,N-dimethylaniline–1,3,5-trinitrobenzene in chloroform which Ross and Labes[14] have studied under the above conditions and also where [D] = [A]. They explained the observed differences in terms of the formation of 2:1, 1:2 as well as 1:1 complexes described by Eq. 1.

TABLE 1. VALUES FOR THE APPARENT ASSOCIATION CONSTANT K_c AND EXTINCTION COEFFICIENT ϵ FOR TWO CHARGE-TRANSFER COMPLEXES IN VARIOUS SOLVENTS

Tetrachlorophthalic anhydride–hexamethylbenzene[a]

Solvent	K_c (l. mole^{-1})	ϵ
Carbon tetrachloride	14·0	1700
Dibutyl ether	13·0	1800
Benzotrifluoride	6·4	1500
Flurobenzene	2·7	1750
Cyclohexanone	2·4	1800
Benzene	2·3	1950

N,N-Dimethylaniline–1,3,5-trinitrobenzene[b]

Solvent	K_c (l. mole^{-1})	ϵ
Cyclohexane	9·6	1300
n-Hexane	8·2	1120
n-Heptane	8·2	1180
Decalin	7·2	1300
Carbon tetrachloride	3·4	1340
Chloroform	1·3	1140

[a] J. Czekalla and K. O. Meyer, *Z. Physik. Chem.* 27, 185 (1961).
[b] Ref. 25.

TABLE 2. VALVES OF THE APPARENT ASSOCIATION CONSTANT K_c AND EXTINCTION COEFFICIENT K_c FOR THE COMPLEX N,N-DIMETHYLANILINE (D)–1,3,5-TRINITROBENZENE (A) IN CHLOROFORM AT 24·8°[a]

Ratio A:D	K_c (l. mole^{-1})	ϵ	$K_c \,.\, \epsilon \times 10^{-3}$
$5.8 \times 10^{-4} - 7 \times 10^{-3}$	0·62	1800	1·11
$8{\cdot}0 \times 10^{-3} - 2{\cdot}2 \times 10^{-2}$	0·79	1470	1·16
11 – 64	1·18	954	1·13
1	1·91	608	1·16

[a] Ref. 14.

Although K_c varied according to the condition [D] $\gg$, $\ll$ or equal to [A], the product $K_c \,.\, \epsilon$ remained constant, (Table 2). Recently Person has emphasized this constancy of $K_c \,.\, \epsilon$.[15] We shall refer to this point again later.

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[14] S. D. Ross and M. M. Labes, *J. Amer. Chem. Soc.* 79, 76 (1957).

[15] W. P. Person, *J. Amer. Chem. Soc.* 87, 167 (1965).

In comparisons of K_c for naphthalene picrate determined optically[16,17] with those obtained by distribution methods[18] it has been shown that whereas optical determinations[16] in which $[D] \gg [A]$ give values which are ~50% those obtained by distribution studies,[18] when the condition $[D] = [A]$ is used[17] the values of optical measurements are nearly equal to the distribution value; although the optical evaluation has been criticized.[19]

We now question whether the original postulate: that under the experimental conditions normally used, Beer's law is obeyed for the complex. Under typical conditions one component (usually D) may range from 0·1–0·5M in a single determination. If we assume Beer's law, we are assuming that ϵ for the intermolecular charge-transfer transition is independent of a variation in solvent from 0·1M donor to 0·5M donor. Although large variations in ϵ as the solvent is altered are not expected (indeed in the argument above concerning the possible variation in ϵ_{exp} with solvent (Table 1) we have implicitly assumed that ϵ_{true} should not vary by a large factor as the solvent is altered) it seems reasonable to assume that there may be *some* variation. In fact Barb has commented on the possibility of the variation of ϵ with the solvent mixture,[20] although this does not appear to have been followed up. The method of Liptay[19] for evaluating K was claimed to demonstrate the concentration independence of ϵ. However, recently it has been pointed out[21] that a satisfactory evaluation by this method only implies that the shape of the absorption curve is the same for all solutions.

On the supposition that ϵ varies as some function (f) of the excess component, assumed to be D, i.e:

$$\epsilon = \epsilon_0 f[D] \tag{6}$$

where ϵ_0 is the value of the extinction coefficient for an infinitely dilute solution.

In order to see what effect this has in practice, let us assume that this variation can be represented approximately by the linear function:

$$\epsilon = \epsilon_0(1 + \alpha[D]) \tag{7}$$

In the Benesi–Hildebrand evaluation of K_c, Eq. 2 is assumed. If $[D] \gg [A]$ and $[A]$ is the total concentration of acceptor, free and complexed, then:

$$K = \frac{d/\epsilon}{([A] - d/\epsilon) \, . \, [D]} \tag{8}$$

where ϵ is the extinction coefficient of the complex at the wavelength of measurement and d is the corresponding optical density due to absorption by the complex (the system and wavelength are chosen so that the components have no optical absorption at the wavelength of measurement). Eq. 8 may be rewritten:

$$\frac{[A]}{d} = \frac{1}{[D]} \cdot \frac{1}{K_c\epsilon} + \frac{1}{\epsilon} \tag{9}$$

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[16] S. D. Ross and I. Kuntz, *J. Amer. Chem. Soc.* **76**, 74 (1954).

[17] R. Foster, *J. Chem. Soc.* 5098 (1957).

[18] H. D. Anderson and D. LL. Hammick, *J. Chem. Soc.* 1089 (1950); R. Foster, D. LL. Hammick and S. F. Pearce, *J. Chem. Soc.* 244 (1959).

[19] W. Liptay, *Z. Electrochem.* **65**, 375 (1961).

[20] W. G. Barb, *Trans. Faraday Soc.* **49**, 143 (1953).

[21] R. G. Satterfield, *Ber. Bunsenges. Physik. Chem.* **69**, 88 (1965); cf. W. Liptay, *Ber. Bunsenges. Physik. Chem.* **69**, 89 (1965).

This is the Benesi–Hildebrand equation. For a series of solutions a plot of [A]/d against $[D]^{-1}$ should be linear, gradient $K_c^{-1} . \epsilon^{-1}$ and intercept with the ordinate ϵ^{-1}. Figure 1 shows a Benesi–Hildebrand plot for a hypothetical complex where K = 2 l.mole^{-1}; $\epsilon = 1500$; $[A] = 5 \times 10^{-4}$ and $[D] < 0{\cdot}6$M. If Beer's law is obeyed, i.e. if $\alpha = 0$ in Eq. 6, then line I in Fig. 1 is obtained giving the correct gradient and intercept. However if the system had been such that ϵ varied with [D] in the manner described in Eq. 6, for which an assumed value $\alpha = 0{\cdot}2$ is used, then the experimental results when plotted should, apart from experimental scatter still be indistinguishable from a straight line, line II in Fig. 1. The gradient of this line gives the correct product $K_c^{-1} . \epsilon^{-1}$, but the intercept yields a value of $\epsilon = 1810$ instead of 1500; so that the evaluation of K_c from the gradient $K_c^{-1} . \epsilon^{-1}$ is $1{\cdot}6_5$ l.mole^{-1} instead of 2·0 l.mole^{-1}.

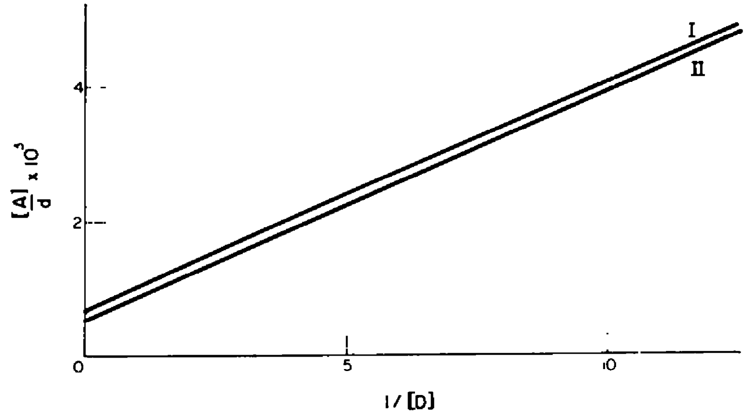

FIG. 1. Benesi–Hildebrand plot for a hypothetical complex ($K_c = 2$ l.mole^{-1}; (I) in which the complex shows no deviation from Beer's law; (II) in which there is a deviation from Beer's law such that $\alpha = 0{\cdot}2$ in Eq. 7.

A similar result is obtained if an alternative plot described by Foster *et al.*[3] is used. Rewriting Eq. 7:

$$d/[D] = -dK_c + K_c[A]\epsilon \qquad (10)$$

Whence for a series of solutions of constant low concentration of A, a plot of d/[D] against d should be linear, with gradient $-K_c$ and intercept with the ordinate equal to $K_c[A]\epsilon$. Plots of the above hypothetical system in terms of Eq. 10 when $\alpha = 0$ and $\alpha = 0{\cdot}2$ are given in Fig. 2.

Although the plot when $\alpha = 0$ is non-linear, the curvature over the experimental range (usually $0{\cdot}1 < d < 0{\cdot}5$) is slight and will not normally be observed because of the scatter of experimental points. In fact a finite curvature for this plot has from time to time been noted.[22] As in the case of the Benesi–Hildebrand plot, the product of $K_c . \epsilon$, now obtained from the intercept with the ordinate, is independent of α.

It is thus seen that small differences in extinction coefficient of a complex between a solution in a pure solvent and in the same solvent but containing significant concentrations of D (or A) can therefore account for relatively large differences in the calculated values of K_c and ϵ, although the experimentally determined product $K_c . \epsilon$ is

[22] R. Foster, unpublished work.

correct. This would account for the constancy of $K_c . \epsilon$ in the determinations made by Ross and Labes,[14] Table 2, although the relative concentrations of D and A are widely varied in different determinations and the resulting separated values of K_c and ϵ show large variations.

A consequence of the solvation theory[12] referred to above, would also predict a constancy in the product $K_c . \epsilon$. However, because in the present proposition, this result comes from the assumption that the fault of the optical methods is due to a failure of Beer's law for the complex species (AD), but that simple mass action relationship, Eq. 1, is tenable, we would expect that values of K_c based on estimates of [AD] by non-optical methods to be correct, whereas the solvation theory would apply equally to optical and non-optical estimations. Recently estimates of [AD] have been made from measurements of chemical shift in the PMR spectra of equilibrium mixtures containing charge-transfer complexes.[23,24] Although the data so far available are limited, the method yields values of K_c commensurate with, but not equal to, those obtained by optical methods. If we assume that the product $K_c . \epsilon$ obtained from optical determinations is correct,* and we evaluate ϵ using the NMR value of K_c, the new values of ϵ are more in accord with the contention that ϵ should increase as K increases,[10,11] (Table 3).

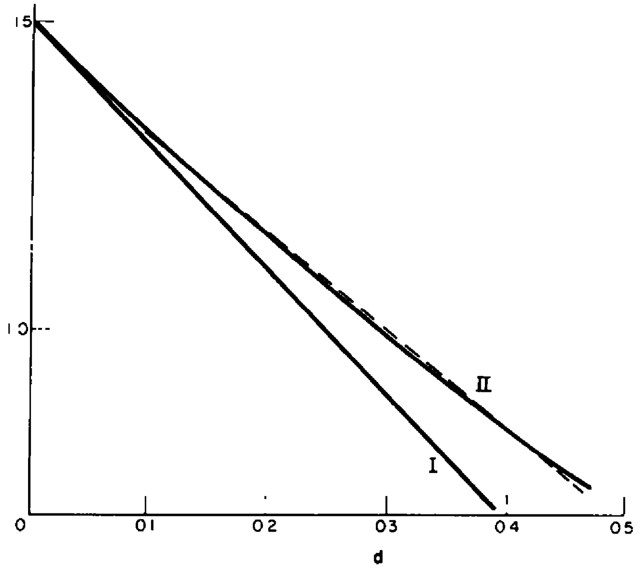

FIG. 2. Foster–Hammick–Wardley plot for a hypothetical complex ([A] = 5 × 10^{-4} M; $K_c = 2\ \text{mole}^{-1}$; $\epsilon = 1500$): (I) in which the complex shows no deviation from Beer's law; (II) in which there is a deviation from Beer's law such that $\alpha = 0{\cdot}2$ in Eq. 7.

In principle the effect of relatively large concentrations of D on the absorption of the complex (AD) when $[A] \ll [D]$ may have its counterpart when $[A] \gg [D]$. Thus

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* Since the product $K_c . \epsilon$ may be accurately determined from optical spectra, there have been redetermined experimentally in Table 3, rather than quoting values of $K_c . \epsilon$ from published values of K_c and ϵ.

[23] M. W. Hanna and A. L. Ashbaugh, *J. Phys. Chem.* **68**, 811 (1964).

[24] R. Foster and C. A. Fyfe, *Trans Faraday Soc.* **61**, 1626 (1965).

in order to minimize this deviation from Beer's law, the optimum condition for measuring K_c by optical methods is when the total concentration of the solute is a minimum for a given measurable concentration of complex: that is, for complexes with 1·1 stoicheiometry, when the condition [A] = [D] is used.[16]

As a further test of this theory, K_c for the system N,N-dimethylaniline–1,3,5-trinitrobenzene in chloroform has been redetermined optically under the conditions [D] $\gg$, $\ll$ and equal to [A] at 33·5°. At this temperature K_c has also been determined under the condition [D] $\gg$ [A] using the NMR method.[24] (It is not practicable with this technique to measure K_c when [D] $\ll$ or equal to [A].) The results of these determinations are given in Table 4 where it is seen that although the optically determined values of K_c depend on the relative values of [D] and [A], it is the value of K_c when [D] = [A] which is equal to the NMR value of K_c. As pointed out above it is under such conditions that the total solute concentration is a minimum and consequently deviations from Beer's law of the kind described will also be a minimum.

TABLE 3. VALUES OF $K_c \,.\, \epsilon$ (OPTICAL); K_c (NMR)[a]; ϵ (OPTICAL)[b]; AND $\epsilon' = \{K_c \,.\, \epsilon$ (OPTICAL)$\}/K_c$ (NMR) FOR COMPLEXES OF METHYLATED BENZENES WITH 1,3,5-TRINITROBENZENE IN CARBON TETRACHLORIDE AT 33·5°

Donor[c]	$K_c \,.\, \epsilon \times 10^{-3}$ (optical)	K_c (NMR)	ε (optical)	ϵ'
Mesitylene	1·74	$0{\cdot}79_7$	3000	2180
Durene	3·33	$1{\cdot}32_0$	2390	2520
Pentamethylbenzene	5·69	$1{\cdot}93_8$	2440	2950
Hexamethylbenzene	9·92	$3{\cdot}30_8$	2500	3100

[a] Ref. 24. [b] N. B. Jurinski and P. A. D. de Maine, *J. Amer. Chem. Soc.* 86, 3217 (1964). [c] Maxima for complexes with benzene, toluene of the xylenes could not be resolved.

TABLE 4. ASSOCIATION CONSTANTS K_c AND EXTINCTION COEFFICIENTS FOR THE COMPLEX N,N-DIMETHYLANILINE–1,3,5-TRINITROBENZENE IN CHLOROFORM AT 33·5°, UNDER DIFFERENT CONCENTRATIONS OF DONOR (D) AND ACCEPTOR (A)

Method	Rel. conc.	K_c (l. mole^{-1})	$\epsilon \times 10^{-3}$	$K_c \,.\, \epsilon \times 10^{-3}$
Optical	[A] $\gg$ [D]	$1{\cdot}0_8$	$0{\cdot}9_8$	$1{\cdot}0_3$
Optical	[A] $\ll$ [D]	$0{\cdot}6_9$ $0{\cdot}6_8$	$1{\cdot}5_7$ $1{\cdot}5_9$	$1{\cdot}0_8$ $1{\cdot}0_8$
Optical	[A] = [D]	$0{\cdot}4_0$	$2{\cdot}6_6$	$1{\cdot}0_5$
NMR	[A] $\ll$ [D]	$0{\cdot}40_5$	—	—

EXPERIMENTAL

Materials were purified as described previously.[25] The method of Foster *et al.*[8] was used to evaluate K_c optically when one component was in large excess, otherwise the method described by Foster[17] was used. The NMR method for evaluating K_c has been described recently.[24]

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[25] R. Foster and D. LL. Hammick, *J. Chem. Soc.* 2685 (1954).