365. *The Evaluation of Equilibrium Constants and Extinction Coefficients for Weak Charge-transfer Complexes*

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New equations for analysing the light-absorption by weak charge-transfer complexes are given which emphasise the role played by solvation. In the theory, there is no need to invoke two types of charge-transfer absorption, one due to "contacts" and one to complexes, as is done in the Mulliken–Orgel theory. It is shown that an analysis of weak complexes, using the Benesi–Hildebrand equation, overestimates ε_c and underestimates K. Also, in a family of related complexes, the expected correlation between K and ε_c is found when the data is re-evaluated.

From Mulliken's[1] original theory of charge-transfer complexes and their spectra, it was predicted that, in general, there should be a relationship between the strength of the complex and the intensity of the charge-transfer bands; the stronger the complex, the more intense should be the bands. In fact, experiment has shown that an inverse relationship between these two quantities is more commonly found, and, for some very weak complexes, very high extinction coefficients have been suggested.

The most common method of determining the stability of a charge-transfer complex

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[1] R. S. Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 600.

and the intensity of the charge-transfer band is that first proposed by Benesi and Hildebrand (B–H).[2] Applying the mass-action law to the equilibrium

$$\mathrm{A} + \mathrm{D} \rightleftharpoons \mathrm{C}$$

i.e.,

$$K = \frac{[\mathrm{C}]}{[\mathrm{D}][\mathrm{A}]} = \frac{[\mathrm{C}]}{(\mathscr{D} - [\mathrm{C}])(\mathscr{A} - [\mathrm{C}])}, \tag{1}$$

where $\mathscr{D}$ and $\mathscr{A}$ are the total concentrations of donor and acceptor, both complexed and uncomplexed, and introducing the usual expression for the optical density of the charge-transfer band

$$\mathrm{O.D.} \equiv [\mathrm{C}]l\varepsilon_c, \tag{2}$$

they derived * the relationship, valid under the condition $\mathscr{D} \gg \mathscr{A}$,

$$\frac{\mathscr{A}l}{\mathrm{O.D.}} = \frac{1}{K\varepsilon_c} \cdot \frac{1}{\mathscr{D}} + \frac{1}{\varepsilon_c}. \tag{3}$$

l is the path-length of the cell and ε_c the extinction coefficient of the complex at some wavelength where neither D nor A absorb. For constant $\mathscr{A}$, a plot of $\mathscr{A}l/\mathrm{O.D.}$ against $1/\mathscr{D}$ gives a straight line of slope $1/K\varepsilon_c$ and intercept $1/\varepsilon_c$.†

The B–H equation seems to fail for very weak complexes. For example, iodine–n-heptane shows an absorption in the region 2000—2600 Å. If this complex is studied in perfluoroheptane,[3] it is found that the intensity of the band increases strictly linearly with the n-heptane concentration. It follows that a B–H plot gives a straight line passing through the origin, which implies that $\varepsilon_c = \infty$, and $K = 0$.

In order to make the B–H equation applicable to weak complexes, Mulliken and Orgel [4] suggested that there were two types of charge-transfer absorption, one associated with real complexes, which satisfy the mass-action law, and the other with DA pairs, which happen to be together just through chance collisions. They introduced an expression giving the concentration of " contact " pairs, [DA]:

$$[\mathrm{DA}] = \alpha'[\mathrm{D}][\mathrm{A}], \tag{4}$$

where α' is the number of sites for a D molecule around any A molecule, multiplied by the apparent molar volume of the solution. They also assumed that the optical density of the " contact " charge-transfer band was given by

$$\mathrm{O.D.} = [\mathrm{DA}]l\varepsilon_{\mathrm{DA}} \tag{5}$$

From these equations, they obtained the expression

$$\frac{\mathscr{A}l}{\mathrm{O.D.}} = \frac{1}{\alpha\varepsilon_{\mathrm{DA}}} \cdot \frac{1}{\mathscr{D}} \tag{6}$$

Mulliken and Orgel concluded that the iodine–n-heptane absorption is an example of pure " contact " charge transfer, and for the iodine–hydrocarbon system there is a mixture of complex and " contact " absorption which is governed by the equation

$$\frac{\mathscr{A}l}{\mathrm{O.D.}} = \frac{1}{K\varepsilon_{\mathrm{ef}}} \cdot \frac{1}{\mathscr{D}} + \frac{1}{\varepsilon_{\mathrm{ef}}}, \tag{7}$$

where

$$\varepsilon_{\mathrm{ef}} = \varepsilon_c + \frac{\alpha'[\mathrm{DA}]}{K}$$

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* Note that a similar expression can be deduced by using mole fractions.

† There are numerous related forms of this equation, but we do not wish to go into their relative merits in this Paper.

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

[3] D. Evans, *J. Chem. Phys.*, 1955, **23**, 1424, 1426, 1429.

[4] L. E. Orgel and R. S. Mulliken, *J. Amer. Chem. Soc.*, 1957, **79**, 4939.

There are two unsatisfactory aspects of the Mulliken–Orgel theory. First, there would appear to be little thermodynamic justification for assuming two kinds of complex, one obeying the mass-action law and the other not. Secondly, no place is given to the role of the solvent in the theory; in the case of weak complexes, the donor is competing with solvent for the sites around the acceptor. It has been observed, not unexpectedly, that K depends on solvent; *e.g.*, Cromwell and Scott [5] found $K = 1{\cdot}9$, $2{\cdot}7$, and $1{\cdot}4$ for iodine–benzene in carbon tetrachloride, benzene, and n-heptane, respectively.

We wish to show that, if the competition between complexing and solvation is allowed for in the theory, there is no need to introduce two kinds of complex, and the behaviour of the weak complexes can be fitted into the same theory as is that of the strong complexes.

There have been earlier treatments of the effect of solvation on complex-formation, which treat the solvent as a competing donor, according to the equilibria

$$\mathrm{D} + \mathrm{A} \rightleftharpoons \mathrm{C} \qquad \mathrm{S} + \mathrm{A} \rightleftharpoons \mathrm{SA}$$

Merrifield and Phillips [6] derived an equation (similar to one used earlier by Corkill *et al.*[7]) which held for the B–H conditions. Tamres [8] derived equations which were slightly more general. However, these equations have not received the prominence they deserve in the study of molecular complexes, and their relevance to the concept of contact charge-transfer spectra has not been emphasised. In this Paper, we shall give a more general treatment of the competition between solvation and complexing, and show how the equations can be used to reinterpret some of the data on weak complexes which are already in the literature.

We start by assuming that the free donor, free acceptor, and complex occur in solution each with a well-defined solvation shell. In this case, complex-formation is governed by an equilibrium of the form

$$\mathrm{AS}_n + \mathrm{DS}_m \rightleftharpoons \mathrm{DAS}_p + q\mathrm{S}, \tag{8}$$

where $q = n + m - p$. We define an equilibrium constant for this by ($\mathrm{C} \equiv \mathrm{DAS}_p$):

$$K = \frac{[\mathrm{C}]x_{\mathrm{S}}{}^{q}}{[\mathrm{AS}_n][\mathrm{DS}_m]}, \tag{9}$$

where x_{S} is the mole fraction of free solvent defined relative to the total number of moles of D, A, and S (complexed and uncomplexed):

$$x_{\mathrm{S}} = \frac{[\mathrm{S}]}{\mathscr{S} + \mathscr{D} + \mathscr{A}} \tag{10}$$

K is defined in this way so that it has the same dimensions as the B–H equilibrium constant. Under the B–H conditions ($\mathscr{D} \gg \mathscr{A}$), this will lead to the equation [cf. equation (3)]

$$\frac{\mathscr{A}l}{\mathrm{O.D.}} = \frac{1}{\mathscr{D}} \cdot \frac{x_{\mathrm{S}}{}^{q}}{K\varepsilon_{\mathrm{c}}} + \frac{1}{\varepsilon_{\mathrm{c}}}, \tag{11}$$

which differs from the B–H equation only by the inclusion of the mole fraction of free solvent.

Analysis of data with the B–H equation amounts to the assumption that, for constant $\mathscr{A}$, an increase in $\mathscr{D}$ does not lead to a change in x_{S}. This is clearly not the case; as more donor is added to a given solution of A, it is necessary to remove solvent in order to keep $\mathscr{A}$ constant, and also free solvent is taken up by solvation of the donor. Let $\mathscr{S}_0$ be the total

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[5] T. M. Cromwell and R. L. Scott, *J. Amer. Chem. Soc.*, 1950, **72**, 3825.

[6] R. E. Merrifield and W. D. Phillips, *J. Amer. Chem. Soc.*, 1958, **80**, 2779.

[7] J. M. Corkill, R. Foster, and D. L. Hammick, *J.*, 1955, 1202.

[8] M. Tamres, *J. Phys. Chem.*. 1961, **65**, 654.

concentration of solvent when $\mathscr{D} = 0$. Then, letting λ be the ratio of the molar volume of the donor to that of the solvent, and assuming that there is no volume contraction on mixing, we have

$$\mathscr{S} = \mathscr{S}_0 - \lambda\mathscr{D}$$

and

$$\begin{aligned}[\text{S}] &= \mathscr{S} - n\mathscr{A} - m\mathscr{D} + q[\text{C}]\\ &= \mathscr{S}_0 - (m+\lambda)\mathscr{D} - n\mathscr{A} + q[\text{C}]\end{aligned}$$

If $\mathscr{D} \gg \mathscr{A}$, it follows that

$$x_{\text{S}} = \frac{\mathscr{S}_0 - (m+\lambda)\mathscr{D}}{\mathscr{S}_0 + (1-\lambda)\mathscr{D}} \tag{12}$$

Substituting this into equation (11) leads to the expression

$$\frac{\mathscr{A}l}{\text{O.D.}} = \frac{1}{\mathscr{D}}\cdot\frac{1}{K\varepsilon_{\text{c}}}\left(\frac{1-(m+\lambda)\dfrac{\mathscr{D}}{\mathscr{S}_0}}{1+(1-\lambda)\dfrac{\mathscr{D}}{\mathscr{S}_0}}\right)^{q} + \frac{1}{\varepsilon_{\text{c}}} \tag{13}$$

The equilibrium which we are considering, equation (8), is only valid if there is enough solvent to solvate all D, A, and complex, so that a necessary condition is $\mathscr{S}_0 > \mathscr{D}$. Taking only the first term in $\mathscr{D}/\mathscr{S}_0$ in equation (13), we obtain

$$\frac{\mathscr{A}l}{\text{O.D.}} = \frac{1}{\mathscr{D}}\cdot\frac{1}{K\varepsilon_{\text{c}}}\left(1 - q(m+\lambda)\frac{\mathscr{D}}{\mathscr{S}_0}\right)\left(1 - q(1-\lambda)\frac{\mathscr{D}}{\mathscr{S}_0}\right) + \frac{1}{\varepsilon_{\text{c}}}$$

giving

$$\frac{\mathscr{A}l}{\text{O.D.}} = \frac{1}{\mathscr{D}}\cdot\frac{1}{K\varepsilon_{\text{c}}} + \frac{1}{\varepsilon_{\text{c}}}\left(1 - \frac{q(m+1)}{K\mathscr{S}_0}\right) \tag{14}$$

Suppose we have data which has been analysed by means of the B–H equation. Then

$$K_{\text{B–H}} = \frac{\text{Intercept}}{\text{Slope}} = K - \frac{q(m+1)}{\mathscr{S}_0}$$

and

$$\varepsilon_{\text{B–H}} = \frac{1}{\text{Intercept}} = \varepsilon_{\text{c}}\left(\frac{K}{K_{\text{B–H}}}\right)$$

It is clear that a B–H analysis underestimates K by an amount $q(m+1)/\mathscr{S}_0$ and overestimates ε by the ratio $(K/K_{\text{B–H}})$. For strong complexes, $K \gg q(m+1)/\mathscr{S}_0$, and the B–H analysis is valid. The pure " contact " conditions in the B–H analysis, which occur when the intercept is zero, are

$$K = \frac{q(m+1)}{\mathscr{S}_0};\quad \varepsilon_{\text{c}} = \frac{q(m+1)}{\mathscr{S}_0 \times \text{slope}}.$$

It is possible to have such weak complexes that the measured intercept is negative:

$$K < q(m+1)/\mathscr{S}_0$$

There are two conditions which maximise the difference between $K_{\text{B–H}}$ and K; the donor is highly solvated, and a large number of solvent molecules are extruded when the complex is formed. Both of these conditions are likely to occur for large aromatic systems which typically form charge-transfer complexes.

Figures 1 and 2 show the effect of solvation on two series of complexes, both with carbon tetrachloride as solvent ($\mathscr{S}_0 = 10{\cdot}3$); methylbenzenes–iodine and methylbiphenyls–1,3,5-trinitrobenzene. For both series, the B–H analysis gives non-linear and inverse correlations between K and ε. It is seen that, as the value of $q(m + 1)$ is increased, the correlated values of K and ε_c approach a linear relationship, and there is one set in each case for which a plot of K against ε_c is a straight line going through the origin. This is what is expected from the original Mulliken theory of charge-transfer complexes, although the appearance of the staight lines is rather more than one has any right to expect. Figure 3 shows the analogous plots for the series of complexes methylbenzenes–chloranil in carbon tetrachloride. These are curved rather than linear, but, however, still show the predicted relationship between K and ε_c.

Plot of ε_c against K for three series of complexes in carbon tetrachloride, modified according to equation (14)

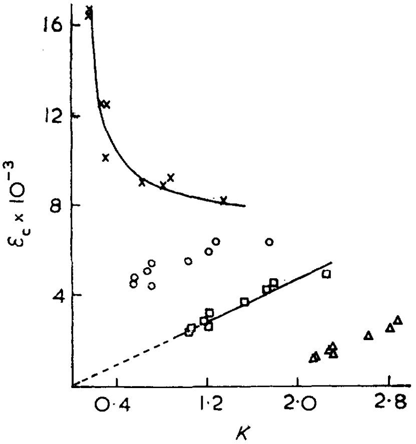

FIGURE 1. Methylbenzenes–iodine
×, $q(m + 1) = 0$ (B–H); ○, $q(m + 1) = 4$; □, $q(m + 1) = 9$; △, $q(m + 1) = 20$

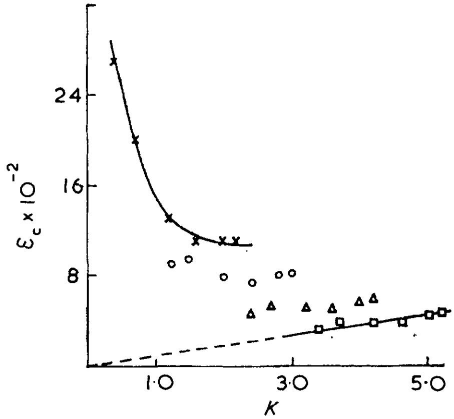

FIGURE 2. Methylbiphenyls–1,3,5-trinitrobenzene
×, $q(m + 1) = 0$ (B–H); ○, $q(m + 1) = 8$; △, $q(m + 1) = 20$; □, $q(m + 1) = 30$

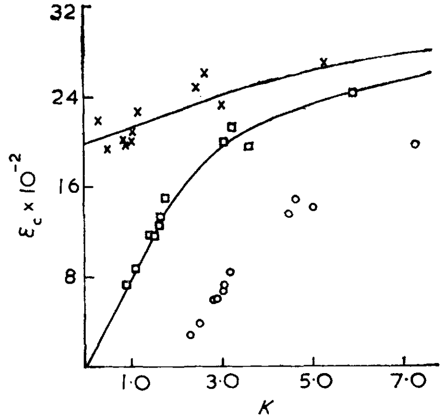

FIGURE 3. Methylbenzenes–chloranil
×, $q(m + 1) = 0$ (B–H); □, $q(m + 1) = 6$; ○, $q(m + 1) = 20$

For the methylbenzene–iodine series, the linear correlation between K and ε_c which passes through the origin occurs for a value of $q(m + 1) = 9$. This is reasonable; one might expect that 2—3 solvent molecules are excluded when the iodine and benzene come together, and that there are 4—5 molecules of carbon tetrachloride solvating each methylbenzene molecule. For the series methylbiphenyls–1,3,5-trinitrobenzene, a value $q(m + 1) = 30$ is necessary to obtain a line through the origin. Biphenyl is about twice as large as benzene, so one would expect $m = 8$—10, and, also, since 1,3,5-trinitrobenzene is larger than iodine, one would expect more solvent molecules to be excluded on complexing in this series.

Because there is bound to be some uncertainty in the best values of $q(m + 1)$, the accuracy to which one can measure ε_c and K for any one complex, in the type of experiment we are discussing, is low [about ±25%, if we adopt the criterion discussed above for obtaining the best values of $q(m + 1)$]. However, the relative values of K and ε_c in the series should be given with just the same accuracy as one expects from the B–H analysis.

The equilibrium constant which we have defined depends on solvent, but ε_c should not; at least, ε_c should show no greater change with solvent than is observed for the absorption bands of molecules in general. Moreover, ε_c should be approximately that which is directly measured by a B–H plot in a gas-phase experiment. In support of our approach, we have the data of Lang and Strong [9] on the benzene–iodine complex in the gas phase, for which they find $\varepsilon_c = 1700$ [if $q(m + 1) = 9$, then we deduce $\varepsilon_c = 2400$, compared with the B–H value of 17,000].

For very weak complexes, it is clearly almost impossible to make a reliable estimate of K and ε_c. For the iodine–heptane case, if we take $q(m + 1) = 10$, then the data of Evans [3] give $\varepsilon_c = 617$ and $K = 2{\cdot}27$.

We conclude with a few comments on the original model. We have assumed that donor, acceptor, and complex have well-defined solvation shells. We mean by this, that there are solvent molecules surrounding these species which are bound in such a way that they cease to behave like free solvent. However, it is not necessary to assume that solvation numbers are equal to the numbers of nearest-neighbour solvent molecules. For example, benzene in carbon tetrachloride might be expected to have about ten nearest neighbours. However, only those which are packed in close to the electron cloud are likely to be strongly bound; those which are on the perimeter of the ring will presumably still behave in a thermodynamic sense like free solvent molecules (benzene and carbon tetrachloride do have a positive heat of mixing, which supports the idea of solvation).

We have shown in this Paper that a satisfactory theory of weak charge-transfer complexes can be based on the idea of competition between solvation and complexing. The model suggested by Orgel and Mulliken, in which there may be two different types of charge-transfer species, complexes and " contacts," in the solution, does not appear to be necessary. Finally, if one is seeking to explain experimental values of K and ε_c on the basis of quantum-mechanical calculations, then these parameters must have been deduced after due consideration of solvation processes.

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[9] F. T. Lang and R. L. Strong, private communication.