A Method for Independent Determination of Equilibrium Constant and Molar Absorptivity of Molecular Complexes from Spectrophotometric Data†

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Synopsis. Two separate equations, one cubic in K and the other quadratic in ε, have been developed for calculating K and ε of molecular complexes independently of each other. The equations on testing with various spectrophotometric data yielded values of K and ε which agree with those obtained by others using well known procedures.

After the important observation of Benesi and Hildebrand[1] and subsequently the interpretation of the phenomenon by Mulliken,[2] several equations[1,3-6] have been derived and tested for the evaluation of equilibrium constants of molecular complexes. The applicability of these equations are, for some obvious reasons,[7] specific. The reported values of K and ε while showing fair constancy among the values obtained by different investigators for strong complexes deviate widely for weak complexes. Various explanations have been suggested[8-19] to account for the observed discrepancies. However, Person[8] has mentioned about some criteria for the reliable determination of equilibrium constant in the case of weak molecular complexes. But this requires a previous knowledge of an approximate value of the equilibrium constant and, due to solubility restriction of the components, it is difficult to fulfil the criteria in all cases. Briegleb[20] and Person[8] indicated that one difficulty in obtaining reliable values of K and ε for weak molecular complexes may be due to the difficulty in the independent determination of K and ε using spectral method, although it is easy to determine the product $K\varepsilon$.

In the present communication we have developed single parameter equations for independent evaluation of K and ε from spectral data, and these equations have been tested for different systems, including strong and weak CT complexes, using the experimental data of various workers from literature.

Principle and Derivation of the Equations

Equation for K Independent of ε. Considering the following equilibrium

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

the equilibrium concentration, C_c, in terms of the equilibrium constant K, is given by

$$C_c = \frac{1+K(C_A^0+C_D^0)-[\{K(C_D^0-C_A^0)\}^2+2K(C_A^0+C_D^0)+1]^{1/2}}{2K} \qquad (2)$$

where C_A^0 and C_D^0 denote the initial concentrations of the acceptor and donor respectively. Substituting $C_c=d/\varepsilon l$ in Eq. 2, we obtain

$$d = \frac{1+Kx-(yK^2+2xK+1)^{1/2}}{2K}\varepsilon l \qquad (3)$$

where $d=d_{obsd}-d_A^0-d_D^0$, $\varepsilon=\varepsilon_C-\varepsilon_A-\varepsilon_D$, l is the optical path length, d's are the optical densities and ε's the molar absorptivities and $x=C_A^0+C_D^0$ and $y=(C_D^0-C_A^0)^2$.

Now, the ratio of the optical densities of the i th and j th solution

$$\frac{d_i}{d_j} = \frac{1+x_iK-(y_iK^2+2x_iK+1)^{1/2}}{1+x_jK-(y_jK^2+2x_jK+1)^{1/2}} \qquad (4)$$

which on rearrangement gives

$$z+(d_ix_j-d_jx_i)K = d_i(y_jK^2+2x_jK+1)^{1/2} - d_j(y_iK^2+2x_iK+1)^{1/2} \qquad (5)$$

where $z=d_i-d_j$. Equation 5, on squaring and rearrangement, yields

$$pK^2+qK+r = r\{(y_jK^2+2x_jK+1)(y_iK^2+2x_iK+1)\}^{1/2} \qquad (6)$$

where

$$p = (d_ix_j-d_jx_i)^2 - d_i^2y_j - d_j^2x_i$$
$$q = 2\{(d_ix_j-d_jx_i)Z - d_i^2x_j - d_j^2x_i\}$$

and

$$r = -2d_id_j = z^2 - d_i^2 - d_j^2.$$

Equation 6 on squaring, rearranging and using the following substitutions

$$a = p^2 - r^2y_iy_j,\ b=2(pq-r^2x_iy_j-r^2y_ix_j),$$
$$g = q^2+2pr-r^2y_i-r^2y_j-4r^2x_ix_j,$$

and $h = 2(qr-r^2x_i-r^2x_j)$,

yields

$$aK^4+bK^3+gK^2+hK = 0$$

or,

$$aK^3+bK^2+gK+h = 0 \qquad (7)$$

Since $K\neq 0$

This cubic equation in K is independent of ε. Equation 7 has been solved numerically by a general method of root determination for real polynomials. The Burroughs system program Library subroutine RLPOLY has been employed for this part, which uses a three-stage variable-shift iteration method developed by Jenkins and Traub.[21] Equation 7 is more general than that developed and used by Nagakura[7] in connection with his studies on amine–iodine systems.

Equation for ε Independent of K. Considering a pair, i th and j th of solutions, we get from the equation

$$K/C_c = \frac{1}{(C_A^0-C_C)(C_D^0-C_c)}$$

an equation

$$\frac{d_j}{d_i} = \frac{S_j\varepsilon^2l^2+d_j^2-d_jx_j\varepsilon l}{S_i\varepsilon^2l^2+d_i^2-d_ix_i\varepsilon l} \qquad (8)$$

where $S=C_A^0C_D^0$. Equation 8, after suitable rearrangement and substitution yields

$$m\varepsilon^2l^2 - n\varepsilon l + f = 0 \qquad (9)$$

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where

$m = d_jS_i - d_iS_j$, $n = d_id_j(x_i - x_j)$, and $f = d_id_j(d_i - d_j)$.

Equation 9 is quadratic in εl and yields

$$\varepsilon = [n \pm (n^2 - 4mf)^{1/2}]/2\,ml \qquad (10)$$

which is independent of K. Only one value of ε is accepted, neglecting the physically inadmissible one.

Results and Discussion

Equations 7 and 10 have been solved by Burroughs 6700 systems using our program for calculating the values of K and ε, independent of one another, of a large number of wide variety of molecular complexes, using the experimental data of different investigators from existing literature. These include the data on strong and weak complexes, wavelength dependence of K and ε and also the effects of solvents. Some representative results are shown in Table 1. The noted differences in many cases may be due to the different approach of the two types of methods. While our procedure evaluates K and ε independent of each other, the reported ones require the separation of K and ε, through the intercept and slope of linear plots, from the product $K\varepsilon$ occurring in the derived equations.

The accuracy of the proposed method like any pairwise evaluation procedure depends on the precision of the experimental data. With precise data our equations yield values of K and ε whose standard deviations lie within 1 to 12%.

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Table 1.

System	K/mol l^{-1}		ε/l mol^{-1} cm^{-1}	
	Our method	Reported	Our method	Reported
TCPA[a]-Phenanthrene[22]	7.5	7.3	712	714
TCPA-Biphenyl[22]	2.6	2.9	552	500
TCPA-Quinoline[22]	30.75	26	130	132
TCPA-2-Methylquinoline[22]	14.6	15	228	226
TBPA[a]-Phenanthrene ($CHCl_3$)[24]	0.8	0.9	612	513
TBPA-Phenanthrene (C_6H_6)[24]	3.49	3.41	470	455
TBPA-Acenaphthene ($CHCl_3$)[24]	2.97	2.8	878	909
TBPA-Acenaphthene (C_6H_6)[24]	1.29	1.46	1084	769
DDQ[a]-Toluene[25]	0.94	0.92	2214	2332
DDQ-Biphenyl[25]	0.95	0.96	1212	1366
DDQ-Phenanthrene[25]	14.15	14.54	2041	2000
DDQ-Fluorene[25]	15.22	14.60	1612	1666
Chloranil-Indole[26]	2.83	2.86	1557	1510
1,3,5-Tricyanobenzene-TMPD[27] [a]	4.07	4.0	369	354
1,3,5-Trinitrobenzene-Diphenylamine[28]	0.5	0.4	1410	1390
ICl-Dioxane (335 nm)[29]	22.94	23.86	814	830
ICl-Dioxane (345 nm)	21.97	23.12	1123	1146
ICl-Dioxane (355 nm)	22.47	23.07	1338	1391
ICl-Dioxane (365 nm)	22.77	23.03	1357	1509
Br_2-Naphthalene[21]	0.235	0.23	5608	5660
I_2-DMA[a] (CH_2Cl_2)[30]	1.32	1.4	661	624
I_2-Naphthalene[31]	0.25	0.26	7479	7250
I_2-Pyrene[32,34] [b]	40	43	143	161
I_2-α-Picoline[33]	50.52	50	1032	1000
I_2-Isoquinoline[33]	40.1	39.4	1607	1538
I_2-Pyridine[33]	47.29	43.74	947	952

a) TCPA: tetrachlorophthalic anhydride, TBPA: tetrabromophthalic anhydride, DDQ: 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, TMPD: *N,N,N',N'*-tetramethyl-*p*-phenylenediamine, DMA: dimethyl acetamide. b) For Pyrene-iodine system the iterative value of K obtained by processing the data in Ref. 32 is 43 mol l^{-1}. The recalculated value of molar absorptivity is 140 l mol^{-1} cm^{-1}.

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