An Alternative Method of Solving the Rose-Drago Equation for the Determination of Equilibrium Constants of Molecular Complexes†

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An alternative method for solving the Rose-Drago equation for the determination of equilibrium constants of molecular complexes has been developed. It yields well-defined K values even for certain systems in which the Rose-Drago procedure for solving the R-D equation is not satisfactory. Our method is based on the transformation of the Rose-Drago equation into one involving three variables and using two linear plots. In applying the method to a wide variety of experimental data, the calculated values of the equilibrium constant have been found to be in excellent agreement with those computed by the well-known iterative procedure. With good data, the calculated values are in good agreement with those from the Benesi-Hildebrand or some other modified plots.

Molecular addition compounds formed by the interaction of electron donors and acceptors are generally characterized by intense electronic absorption attributable to neither component of the addition compound, but to a new molecular species, the compound—usually referred to as the molecular complex — itself. The interpretation of the occurrence of these absorption bands by Mulliken[1] in the light of his charge-transfer theory is now widely accepted. After the formulation of this theory, numerous workers were interested in determining the composition and stability of these complexes. Benesi and Hildebrand[2] formulated a spectrophotometric method and many investigators used it or some modification of it[3,4] to determine the equilibrium constants. Certain limitations of the Benesi-Hildebrand (B-H) method[5] became evident and new equations were derived. Of these, the most noteworthy one is the Rose-Drago equation,[6] which is perfectly general. This equation (Eq. 1; see next section) contains two unknowns, K and ε_c; they are, respectively, the equilibrium constant and the molar absorptivity of the complex. An analytical solution for ε_c could be derived by constructing two simultaneous equations, each representing different experimental trials. Alternatively Rose and Drago[6] developed a graphical procedure for solving their general equation. This consisted of random selection of ε_c values and calculation of K^{-1} from one set of experimental data, namely with one particular value of initial concentration of donor and acceptor, plotting K^{-1} as a function of ε_c, repetition of this procedure with other sets, and finally evaluating K^{-1} and ε_c values from the common point of intersection. But selection of a series of ε_c values at random for each set of experimental data renders this graphical method laborious and sometimes very difficult to employ. In addition, in many cases the Rose-Drago plot shows a wide scatter in the values of K and ε_c.[7]

In the present article, we report an alternative graphical method, based on the consideration of two linear plots, for solving the Rose-Drago equation. This procedure is straightforward, more convenient to use, and can be employed without any loss of generality of the equation.

Principle and Method

Drago and Rose[7] derived Eq. 1 relating K^{-1} and ε_c as

$$K^{-1} = \frac{C_D^\circ C_A^\circ(\varepsilon_c-\varepsilon_A)}{d-d_A^\circ} - C_D^\circ - C_A^\circ + \frac{d-d_A^\circ}{\varepsilon_c-\varepsilon_A}, \quad (1)$$

where C_D° and C_A° are the initial concentrations of the donor and acceptor respectively, ε_A is the molar absorptivity of the acceptor, d_A° is the absorbance of the initial concentration of the acceptor, and d corresponds to the total absorbance at any given wavelength for a cell of 1 cm path length.

Now, Eq. 1 can be written in the form:

$$y = L + Mx - M^2z, \quad (2)$$

where

$$y = \frac{C_A^\circ C_D^\circ}{d-d_A^\circ}, \quad x = C_A^\circ + C_D^\circ, \quad z = d - d_A^\circ,$$
$$L = K^{-1}/(\varepsilon_c-\varepsilon_A),$$

and

$$M = 1/(\varepsilon_c-\varepsilon_A).$$

Now, from definitions, it can be easily shown that z is a linear function of C_c, the equilibrium concentration of the complex, and at the lower range of donor concentration[8] or within the close range of donor concentration it is a reasonably good approximation to assume that C_c is a linear function of x in the range. Thus, to the first approximation, we can substitute $z=mx+n$ in Eq. 2, yielding

$$y = (L-M^2n) + (M-M^2m)x. \quad (3)$$

Equation 3 gives a linear plot of y *versus* x with slope,

$$S = M - M^2m, \quad (4)$$

and intercept,

$$I = L - M^2n, \quad (5)$$

where m and n can be obtained from the slope and intercept of z *vs.* x plot.

Now, from Eq. 4,

$$M = \frac{1\pm\sqrt{1-4mS}}{2m}. \quad (6)$$

The root $(1+\sqrt{1-4mS})/2m$ is discarded because its value differs widely from that given by the approximate equation $y=L+Mx$, and also because it yields inadmis-

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sible values of ε_c. Substituting the value of M from Eq. 6 into Eq. 5, we get L, and finally $K=M/L$ and $\varepsilon_c=M^{-1}+\varepsilon_A$.

Results and Discussion

The Rose-Drago curve for the naphthalene–picric acid system, constructed from the data by Foster,[9] is shown in Fig. 1. As can be seen from the figure, well-defined values of K and ε_c are not obtainable from the plot. We also observed similar scatter in the Rose-Drago curve for the systems pyridine–iodine and 2-methylpyridine–iodine from the data of Nagchandhuri and Basu.[10]

Using our graphical procedure, we have calculated the equilibrium constant and molar absorptivity values of a large number of a wide variety of molecular complexes, using the experimental data of different investigators for different systems, such as the iodine complexes of polycyclic aromatic hydrocarbons[11] and aza-aromatics,[10] complexes of tetrachlorophthalic anhydride (TCPA) with aza-aromatics,[12] the naphthalene–picric acid complex,[9] and the chloranil–indole complex.[13] A representative linear plot of z *vs.* x and of y *vs.* x for the systems naphthalene–picric acid, iodine–pyridine, and TCPA–quinoline are shown in Figs. 2 and 3 respectively. In all other cases examined by us reasonably good linearity was obtained in these two plots. The calculated values of K and ε_c of various systems are presented in Table 1, which also contains, for comparison, the values of these quantities obtained by various authors by applying either the Benesi-Hildebrand or some other modified plot. We have also computed the values of K and ε_c of these systems with the help of the iterative technique as followed by Arnaud and Bonnier.[14] The iteratively computed values of K, computed by the IBM 1130 computer, are also presented in Table 1. In almost all the cases we examined, the values of K obtained by our procedure are in very good agreement with those obtained by the iterative procedure. Except in the case of TCPA–

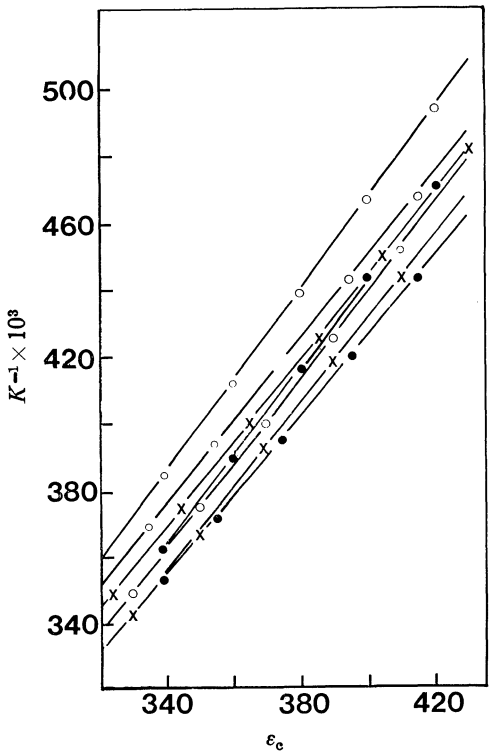

Fig. 1. Rose-Drago plot for the picric acid–naphthalene system. The different lines correspond to the different experimental trials, each a definite value of C_A° and C_D°.

aza-aromatic systems we failed to obtain a reasonably good common point of intersection by the Rose-Drago procedure for the systems under consideration. In the case of the pyrene–iodine complex a K-value of 43 l mol^{-1} with a standard deviation of ± 7 was obtained by Drago and Rose[7] by applying their own procedure. Calculation by our method yields $K=42.9$ l mol^{-1}. For the biphenyl–iodine complex the Rose-Drago procedure yields $K=0.39\pm 0.15$, whereas the reported value is 0.37;[11] our method gives $K=0.28$. For the naphthalene–

Table 1. Equilibrium constants and molar extinction coefficients (ε_c) of various molecular complexes

System	K(l mol^{-1})			ε_c	
	Our method	Iterative method	B-H or modified plot	Our method	B-H or modified
TCPA+Quinoline	29.00	29.86	26.0[a]	132	—
TCPA+2-Methylquinoline	13.13	13.48	15.0[a]	226	—
TCPA+Benzo[*h*]quinoline	19.00	19.14	18.0[a]	300	—
Iodine+Pyridine	38.98	40.37	43.74[b]	1006	952[b]
Iodine+2-Methylpyridine	46.37	48.57	50.00[b]	1043	1000[b]
Iodine+2,6-Dimethylpyridine	29.64	31.95	26.23[b]	878	888[b]
Iodine+Quinoline	66.75	65.07	69.0[b]	2994	3046[b]
Iodine+Isoquinoline	40.07	39.95	39.4[b]	1551	1538[b]
Iodine+Phenanthridine	47.24	46.48	47.0[b]	852	852[b]
Indole+Chloranil	2.82	2.87	2.86[c]	1527	1510[c]
Naphthalene+Picric acid	2.38	2.40	2.29[d]	366	377[d]
Iodine+Pyrene	42.91	42.82	36.49[e]	140	161[e]
Iodine+Biphenyl	0.28	0.29	0.37[e]	5231	4000[e]
Iodine+Naphthalene	0.21	0.21	0.62[e]	6557	2395[e]
Iodine+Phenanthrene	2.67	2.61	1.06[e]	618	1492[e]

a) Ref. 12. b) Ref. 10. c) Ref. 13. d) Ref. 9. e) Ref. 11.

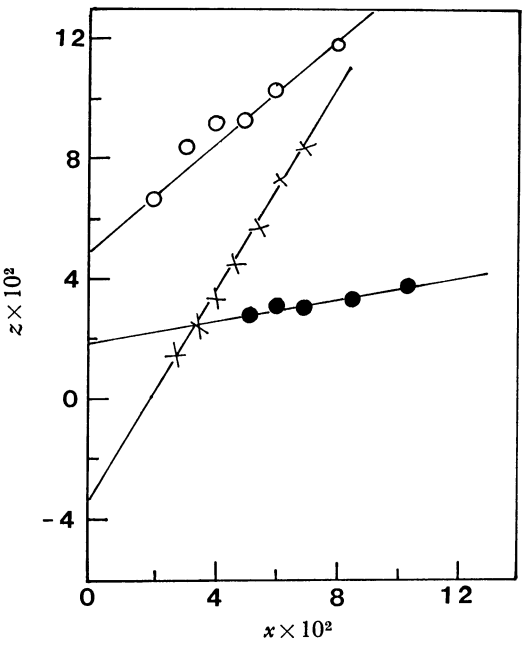

Fig. 2. z *vs.* x plot for the system TCPA–quinoline (●), picric acid–naphthalene (×), and iodine–pyridine (○).

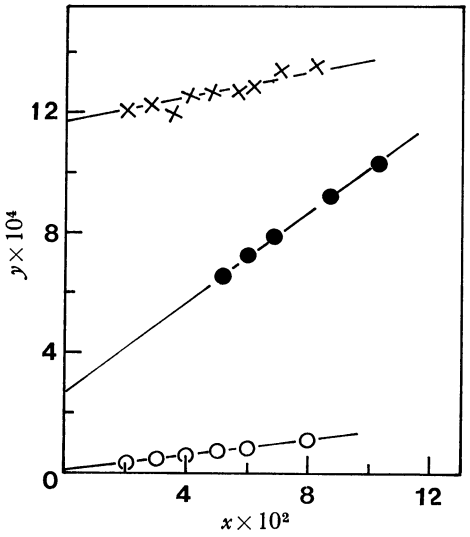

Fig. 3. y *vs.* x plot for the system TCPA–quinoline (●), picric acid–naphthalene (×), and iodine–pyridine (○).

iodine complex the recalculated K by our method is 0.21 which is close to the value, 0.25, quoted by Drago.[7] The K value of 0.62 for this system, obtained by Bhattacharya and Basu[11] from the Benesi-Hildebrand plot, is considerably higher. For the iodine–anthracene system the Rose-Drago equation, solved by our method, yields a much lower value of K than that obtained by Bhattacharya and Basu.[11] This might be due to some specific assumptions in deriving the Benesi-Hildebrand equation rendering it unsuitable for general application.[15]

Drago and Rose[7] felt that a recalculation with many reported data was necessary for yielding meaningful thermodynamic quantities from spectrophotometric investigations. These calculations can be carried out by our procedure for solving the Rose-Drago equation more easily and effectively than by their own graphical procedure.

From the excellent agreement of computed results between our procedure and the iterative procedure, it is apparent that our one-step approximation of linearity between C_c and x is somehow almost equivalent to successive approximations in the process of iteration.

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