vicinity of the ring. This model has the merit that increasing electronegativity or vacant d orbitals leads to increased transfer of π-cloud in the direction of the metal ion. This postulated model can account for the stabilities found.

Cowdrey and Davies[23] have stated that the diazotized anisidines are more stable than benzenediazonium salts which are more stable than diazotized *o*-toluidine. Nesmeyanov's[3] data indicate that those compounds having a group on the ring which allows delocalization of an electron pair are generally the most thermally stable. A metal–diazonium ion interaction as postulated above would assist in the flow of electrons from the amino nitrogen and increase stability. However, as such an interaction increases in strength (increasing electronegativity of the metal atom) flow of electrons from the vicinity of the $C-N_2^+$ bond should also increase with the positive charge on the diazonium group resisting this. The result is decreased electron density in the $C-N_2^+$ bond and its becoming weakened. The delocalization of the amino group electron pair and the decrease of electron density in the above bond have opposite effects. When the pull of electrons away from the $C-N_2^+$ bond becomes large the net effect is destabilization. Considering the effect of water, only the iron compound is less stable than the *p*-dimethylaminobenzenediazonium chloride. In this study only the iron compound has incomplete outer orbitals (3d). These are well known for their coördination of electrons.

The variation of the frequency for the out-of-plane ring hydrogen wag suggests an interaction as proposed. An explanation of Table III is offered by the assumption that the metal ions position themselves over the center of the ring and in the case of the two most stable compounds the metal ions are closer to one side of the ring than the other.

TABLE III

ABSORPTION FREQUENCIES FOR RING HYDROGEN WAGGING

Metal of the compd.	Cm.$^{-1}$	% Trans.
None	818	11.6
Fe	817	10.0
Bi	820	25.0
Zn(2H_2O)	823	26.0
Zn(H_2O)	824	18.8
Sn	826	37.0
Hg	817	11.5
Zn	821	38.5
	833	45.0
Cd	818	42.0
	829	57.5

In spite of the failure to "stabilize" with some of the metal chlorides used, it seems that the present data should be extended to include more metal ions. It is also suggested that greater insight into the interaction of metal ion with diazonium ion may be available through nuclear magnetic resonance spectroscopy.

NEW ORLEANS, LA.

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[23] W. A. Cowdrey and D. S. Davies, *Quart. Rev.*, **6**, 358 (1952).

[CONTRIBUTION FROM THE W. A. NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Molecular Addition Compounds of Iodine. I. An Absolute Method for the Spectroscopic Determination of Equilibrium Constants

BY NORMAN J. ROSE AND RUSSELL S. DRAGO

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A general equation is derived for evaluating acid–base equilibria from spectroscopic data. The equation is a general one and can be applied to any acid–base system that absorbs in some region of the spectra. Application to base–iodine systems is described. The treatment requires fewer assumptions than are involved in the Benesi–Hildebrand treatment or several reported modifications of it. In this article the equation is derived, its application illustrated and the interpretation of reported data evaluated. The advantages of employing our treatment are outlined.

Introduction

The interaction between Lewis bases and iodine provides an ideal system for investigating the basicity of various electron pair donors. The addition compounds formed with iodine are soluble in nonpolar solvents so their heats of formation can be determined in the absence of crystal lattice effects or extensive solvation by studying the equilibrium constant of the reaction $[B + I_2 \rightleftarrows BI_2]$ as a function of temperature. These data usually are obtained from the ultraviolet spectra of the solutions. The equilibrium constant often is calculated by the method proposed by Benesi and Hildebrand[1] or some modification of it.[2-4]

In many of these studies, conclusions and explanations for observed trends are based on small differences in the heats of formation. The slight curvature obtained in the plot of ln K *vs.* $1/T$ was used[5] as evidence to support existence of several geometrical isomers. Scott[6] has been concerned with the effect of solvent on these equilibria and has obtained slightly different values for the equilibrium constant for the reaction $C_6H_6 + I_2 \rightleftarrows C_6H_6 \cdot I_2$ in carbon tetrachloride and in pure benzene as the solvents. DeMaine,[7] on the other hand, reports no solvation effects for the equilibrium between ethanol and iodine.

In view of the importance of conclusions based on small differences in the values for the constant

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[1] H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949).

[2] J. A. A. Ketelaar, *et al.*, *Rec. trav. chim.*, **71**, 1104 (1952).

[3] S. Nagakura, THIS JOURNAL, **76**, 3070 (1954); **80**, 520 (1958).

[4] R. M. Keefer and L. J. Andrews, *ibid.*, **74**, 1891 (1952).

[5] L. E. Orgel and R. S. Mulliken, *ibid.*, **79**, 4839 (1957).

[6] T. M. Cromwell and R. L. Scott, *ibid.*, **72**, 3825 (1950); R. L. Scott, *Rec. trav. Chim.*, **75**, 787 (1956).

[7] P. A. A. DeMaine, *J. Chem. Phys.*, **26**, 1192 (1957).

and for the heats, we were prompted to undertake a rigorous treatment of the experimental data with the intent of eliminating some of the assumptions involved in the other methods for evaluating the data. This paper will be concerned with the derivation of a general method for rigorously treating spectrophotometric data for any acid–base system. The techniques for employing this method to donor–iodine systems will be demonstrated, as will the advantages connected with using this procedure. The cases demonstrated provide additional information indicating that a re-examination of some conclusions based on calculations reported in the literature must be undertaken.

In the second paper in this series the general equation derived here will be applied specifically to donor–iodine equilibria in which the Benesi–Hildebrand equation has been used incorrectly. Errors of the order of magnitude of 10 to 20% have been introduced into the equilibrium constant value.

Discussion

The general equation for the equilibria involved is

$$\mathrm{D} + \mathrm{A} \rightleftarrows \mathrm{DA} \qquad (1)$$

where D is an electron pair donor and A an electron pair acceptor. The equations to be presented are general for any Lewis acid–base reaction but the discussion will be confined to donor–iodine equilibria

$$\mathrm{D} + \mathrm{I_2} \rightleftarrows \mathrm{DI_2} \qquad (2)$$

The equilibrium constant expression for this reaction is

$$K_c = \frac{[C_c]}{[C_D - C_c][C_I - C_c]} \qquad (3)$$

where C_c = concentration of the complex (DI_2) at equilibrium; C_D = initial concentration of the base and C_I = initial concentration of iodine.

There are two regions of the ultraviolet spectra in which the absorption is directly related to the concentration of the complex: the "charge transfer" absorption (often around 240 to 300 mm.) and the "blue shift" absorption (around 460–480 mm.).[8]

When the donor molecule does not absorb in the region studied, equation (4) shows the relationship of the total absorbance (A) to the iodine concentration and to the complex concentration, at any given wave length for a 1 cm cell.

$$A = \epsilon_c C_c + \epsilon_I\,[I_2] \qquad (4)$$

where ϵ_c = molar absorptivity for the complex, ϵ_I = molar absorptivity of iodine and $[I_2]$ = concentration of uncomplexed iodine at equilibrium. In the case of the charge transfer band or a blue shift band separated from the free iodine band the last term in equation 4 drops out because $\epsilon_I = 0$.

When only one complex is formed, equation (5) is also characteristic of the system

$$C_I = C_c + [I_2] \qquad (5)$$

Several investigators have modified and combined these basic equations (equations 3, 4, 5) in various ways but a direct solution for K is not possible from one set of data. Two unknowns (K and ϵ_c) are always present. One approach described by Benesi and Hildebrand (subsequently referred to as B–H) results in the final equation

$$\frac{C_I b}{A} = \frac{1}{K\epsilon_c}\,\frac{1}{C_D} + \frac{1}{\epsilon_c} \qquad (6)$$

where b = breadth of cell. In the following discussion it will be assumed that $b = 1$. In treating experimental data, A should be replaced by A/b for cases in which $b \neq 1$. Equation 6 is that of a straight line whose intercept is $1/\epsilon_c$ and whose slope is $1/K\epsilon_c$. Small values of K are very much dependent upon the extrapolation so the line must be constructed by a least squares method.

Ketelaar, *et al.*,[2] have modified equation 6 to apply in the case of overlapping bands. It will be shown that both of the above treatments are merely special cases of a more reliable approach.

Derivation of an Absolute Equation.—If equation 3 is expanded

$$K = \frac{C_c}{C_D C_I - C_c C_I - C_D C_c + C_c^2} \qquad (7)$$

Eliminating (I_2) between equations 4 and 5 allows the absorbance to be expressed as

$$A = C_c(\epsilon_c - \epsilon_I) + \epsilon_I C_I \qquad (8)$$

If A^0 corresponds to the absorbance of the initial concentration of iodine, then according to Beer's law, $A^0 = \epsilon_I C_I$ and then

$$A = C_c(\epsilon_c - \epsilon_I) + A^0 \qquad (9)$$

Equation 9 is solved for C_c and C_c then is eliminated between this solution and equation 7. After simplification equation 10 can be obtained

$$K^{-1} = \frac{A - A^0}{\epsilon_c - \epsilon_I} - C_I - C_D + \frac{C_D C_I\,(\epsilon_c - \epsilon_I)}{A - A^0} \qquad (10)$$

When experimental conditions are such that the term $[(A - A^0)/(\epsilon_c - \epsilon_I)] - C_I$ is negligible compared to $C_D C_I/(A - A^0)(\epsilon_c - \epsilon_I) - C_D$ equation 10 reduces to a form of the Ketelaar equation

$$\frac{C_I}{A - A^0} = \frac{1}{K(\epsilon_c - \epsilon_I)}\,\frac{1}{C_D} + \frac{1}{\epsilon_c - \epsilon_I} \qquad (11)$$

(to get equation 11 multiply left member of equation 3 in reference 2 by C_I/C_I.)

When at a given wave length absorption bands do not overlap, as is commonly the case for the charge transfer band, A^0 and ϵ_I are zero and equation 10 becomes

$$K^{-1} = \frac{A}{\epsilon_c} - C_I - C_D + \frac{C_D C_I}{A}\,\epsilon_c \qquad (12)$$

When the terms $A/\epsilon_c - C_I$ can be neglected, equation 12 reduces to a form of the B–H equation 6.

The general equation 10 contains two unknowns in the iodine system, K^{-1} and ϵ_c. If two equations like 10 are set up each representing different experimental trials (*i.e.*, C_D and C_D', A and A') an analytical solution can be derived specifically for ϵ_c. Because this expression was awkward to use, a graphical procedure was developed. This more convenient method requires the selection of various values of ϵ_c at random for a given set of experimental data and calculation of the corresponding values of K^{-1}. The values of K^{-1} and ϵ_c (for this one set of experimental values) are plotted as the ordinate and abscissa, respectively, and a curve constructed.

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[8] R. S. Mulliken, This Journal, **74**, 811 (1952); *Rec. trav. chim.*, **75**, 845 (1956), and papers referenced therein.

Similarly, a second set of experimental values is employed and a curve of K^{-1} *vs.* ϵ_c again constructed. When several sets of experimental data have been obtained, all of the curves are plotted on one figure. Ideally they should all intersect in one point for there is only one K and one ϵ_c for the system. In practice, however, the points representing the intersection of any two curves tend to cluster in a relatively small area if the data are good. If each of these points is given equal weight, their mean can be used as the reported value. This procedure is equivalent to solving simultaneous equations[3] for all possible pairs of data.

The general equation can be used for determining equilibria with: (1) the charge-transfer band (no overlap) using equation 12, (2) the blue shift band when there is overlap, using equation 10, (3) the iodine band, using equation 10 for the case where there is overlap with the complex band, (4) ultraviolet, visible and infrared spectra for any acid–base system in which a 1:1 complex forms and the absorption is related to the concentration of the complex either directly or inversely. Equations for stoichiometry other than 1:1 can be derived and treated similarly.

The only assumption involved in the derivation of the above equation 10 is that there are at most two absorbing species which obey Beer's law in the concentration range employed. The isosbestic point can be used as evidence that only two absorbing species are present. The equilibrium constant calculated is a concentration constant, for activity coefficients generally are not known in these systems.

When all of the terms in equation 10 are retained, they must have the same concentration units (*i.e.*, C_D, C_I, ϵ_c and ϵ_I, must be based on either molarity or mole fraction). The mole fraction constant obtained has the same units as, and can be compared with, the B–H constant obtained by expressing C_D in terms of mole fraction, C_c, C_I in molarity units and ϵ_c in l./mole.

Calculations and Results

(A) Benzene–Iodine System.—The original data of Benesi and Hildebrand[1] on the benzene–iodine system in CCl_4 as a solvent were recalculated using the form of equation 10 that applies to this system, *i.e.*, equation 12. Table I contains sample results of calculations for benzene mole fraction $C_D = 0.213$, $C_I = 17.4 \times 10^{-5}$ mole/l. and $A = 0.7076$ (all measured values).

TABLE I

ϵ_c	$\frac{C_D C_I}{A}$	K_x^{-1}
13,000	0.6808	0.468
13,500	.7070	.494
14,000	.7332	.520
14,500	.7594	.546
15,000	.7856	.572
15,500	.8117	.599
16,000	.8379	.625

Preliminary calculations indicated that $A/\epsilon_c - \epsilon_I$ expressed in mole fraction units could be neglected from the general equation 12. Thus C_I, C_c and ϵ_c can be based on moles/l. A curve illustrating the dependence of K on ϵ_c under the above set of experimental conditions thus is obtained. Similar calculations for other sets of experimental data on this system yield a series of curves the coördinates of whose intersections represent solutions for K and ϵ_c (see Fig. 1). The majority of the intersections occur in a small area indicating good experimental precision. The formation of a 1:1 complex is given strong support. Equilibrium constants and the molar absorptivity for the complex were determined for all intersections, and the average deviation was calculated. All values that lay outside the average deviation by a factor of 2.5 were eliminated and a new average determined. The significant data are reported in Table II and values for the equilibrium[9] constant ($K_x = 1.78 \pm 0.05$) and absorptivity of the complex ($\epsilon_c = 15{,}400 \pm 600$ l. mole^{-1} cm.$^{-1}$) were obtained. These results are in good agreement with the values reported by Benesi and Hildebrand $K_x = 1.73$ and $\epsilon_c = 15{,}400$ l. mole^{-1} cm.$^{-1}$.

TABLE II

Sets of C_D	K_x^{-1}	ϵ_c	Sets of C_D	K_x^{-1}	ϵ_c
0.0433–0.213	0.520	14,000	0.924–0.0433	0.574	15,350
.0862– .213	.572	15,000	.924– .0862	.600	15,600
.0433– .619	.571	15,275	.924– .213	.610	15,700
.0862– .619	.602	15,675	1.00 – .924	.500	14,575
.213 – .619	.620	15,890	1.00 – .0433	.572	15,275
.0433– .812	.590	15,725	1.00 – .619	.572	15,275
.0862– .812	.620	16,050	1.00 – .0862	.595	15,500
.924 – .619	.591	15,500	1.00 – .213	.605	15,580

Scott[6] has recalculated the above data[1] using a modified extrapolation procedure. The values $K_x = 1.9$ and $\epsilon_c = 14{,}000$ were obtained. Using a value of $\epsilon_c = 14{,}000$, and Benesi and Hildebrand's data in pure benzene, he recalculated K_x obtaining a value of 2.3. The difference between the value of 2.3 and 1.9 was attributed to solvent effects. Within experimental error examination of the data in Table II fails to show any concentration dependence to K_x. When our value of $\epsilon_c = 15{,}400$ is used to solve the same data in pure benzene the values 1.74, 1.71 and 1.71 are obtained for K_x in good agreement with the values in carbon tetrachloride. The value for K_x in pure benzene is much more dependent on the accuracy of ϵ_c than those in dilute solution and accounts for the differences obtained by Scott. This indicates that any solvent effect by benzene in the concentration ranges of mole fraction 0.02 to 1 lies inside the experimental error and cannot be detected. There is a very definite possibility that a solvent effect may be observed when results obtained when the benzene is not in large excess of the iodine are compared with those obtained at large benzene–iodine ratios. This treatment indicates that for dilute iodine solution, 0.02 *M* solutions of benzene are nearly as effective as pure benzene in causing solvation.

The above system is an example of conditions under which the general equation reduces to the B–H equation. The results obtained are in good agreement when the B–H curve is constructed using a least squares treatment. In the second

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(9) K_x refers to the equilibrium constant obtained when the base concentration is expressed in terms of mole fraction. It is dimensionless. K_c has the dimensions of l. mole^{-1}.

paper in this series, systems will be discussed in which an evaluation by the absolute method is essential. Even in those cases where similar results are obtained, our method has several advantages.

(1) Though in certain cases the B–H equation in conjunction with a least squares method provides results with as good a precision as our rigorous method, we feel the latter is simpler to employ.

(2) The method of Nagakura requires the solution of two simultaneous equations employing data collected under different experimental concentrations of the base. When several base concentrations are employed all combinations of pairs must be used and the equilibrium constant calculated in order to utilize all the measurements. In our method all possible combinations are obtained graphically. A poor set of data can be very easily noticed and eliminated from the final result.

(3) The results are presented graphically in our method and by inspection one can qualitatively determine the precision. The curves obtained can be used as a guide to indicate the best set of experimental conditions for obtaining lines with different enough slopes to make the results significant. Differentiation of equation 10 with respect to ϵ_c indicates that the slope of the K^{-1} *vs.* ϵ_c curves in the region used is largely determined by the term $C_DC_I/(A-A^0)$. Therefore, experimental conditions should be selected that give rise to different values for this term.

(4) This treatment will produce valid equilibrium constants for those acid–base reactions in which the reaction does not go to completion in the pure solvent. The assumption of completeness of reaction is inherent in the B–H extrapolation.

(5) In the Benesi–Hildebrand method it is necessary to assume that the extinction coefficient of the complex is a constant independent of base concentration and the bulk dielectric constant of the solvent. Trends in the values for ϵ_c and K^{-1} as a function of concentration are readily apparent in our treatment if they exist.

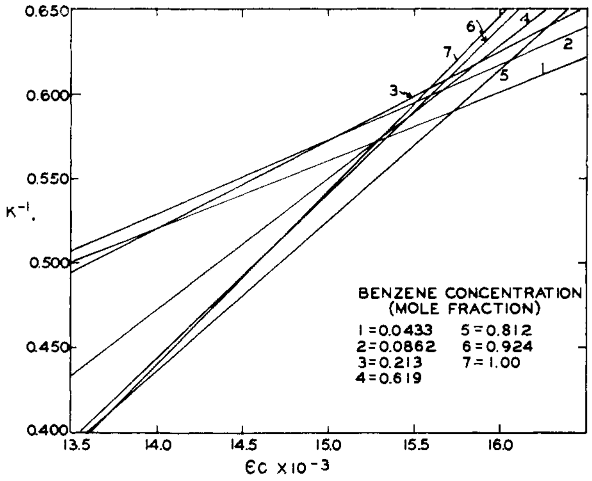

Fig. 1.

Use of our equation eliminates several objections reported in the literature[10,11] which cast doubt on the validity of thermodynamic data calculated by the method of Benesi and Hildebrand. The fact that the results obtained by a B–H calculation agree with those obtained by our more rigorous treatment gives added support to the B–H assumptions in the above cases.

Acknowledgments.—The authors wish to acknowledge helpful discussions with Dr. T. L. Brown and Mr. Larry Sacks on this problem.

[10] L. S. Andrews, *Chem. Revs.*, **54**, 713 (1954).

[11] S. P. McGlynn, *ibid.*, **58**, 1113 (1958).

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[Contribution from the W. A. Noyes Laboratory of Chemistry, University of Illinois]

Molecular Addition Compounds of Iodine. II. Recalculation of Thermodynamic Data on Lewis Base–Iodine Systems Using an Absolute Equation

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The general equation developed in the preceding paper in this series is applied to several sets of reported data. It can be shown that incorrect application of the Benesi–Hildebrand equation to the trimethylamine–iodine system has introduced error into calculated values of the equilibrium constant. A set of data is discussed in which the authors were able to calculate an equilibrium constant by the Benesi–Hildebrand method but which can be shown to be without any significance by our treatment. Finally, it will be demonstrated that in the dioxane–iodine system much more information can be obtained from the data by using our treatment instead of those previously employed.

Introduction

In the first article in this series[1] a general equation was developed to treat spectrophotometric data of acid–base equilibria and a method for solving the equation was presented. This paper will deal with acid–base equilibria to which the Benesi–Hildebrand and related treatments have been incorrectly applied resulting in errors of the order of magnitude of 10 to 15% in the value of the equilibrium constant.[2,3] In another instance, reported[3] data were calculated incorrectly and can be shown to be meaningless when interpreted on the basis of a 1:1 complex.

Discussion

There are several approaches which have been used to evaluate equilibrium constants from the

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[1] N. J. Rose and R. S. Drago, This Journal, **81**, 6138 (1959).

[2] S. Nagakura, *ibid.*, **80**, 520 (1958)

[3] R. Bhattacharya and S. Basu, *Trans. Faraday Soc.*, **24**, 1286 (1958).