

Spectral and Solubility Studies of Molecular Complex Equilibria. Concentration Scale Dependence and Activity Coefficient Effects¹

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Abstract: Difficulties in the investigation of weak molecular complexes in solution are discussed, including the concentration scale dependence of complex formation constants and absorptivities obtained from Benesi–Hildebrand type methods. Activity coefficient effects are considered explicitly for the various techniques which have been used to determine equilibrium constants. It is shown that unambiguous values of activity coefficients of weak molecular complexes in dilute solution can be inferred by combining the results of spectral and solubility experiments. The concentration dependence of activity coefficients and the transfer free energy fractions are reported for several aromatic donor–iodine complexes in heptane at 25°.

Use of the Benesi–Hildebrand (B–H) equation,² related equations,³ and their modifications³ has been widespread in the study of molecular complexes. (See Appendix.) Unfortunately, reports of ambiguities and of serious difficulties with the use of B–H type relations have caused questions as to the meaning and validity of results from these calculations. For example, many workers have observed that the choice of concentration scale may strongly influence the values of the formation constant (K) and the absorptivity (ϵ) derived from B–H type relations.^{4–8} Thus, values of K based on different concentration scales are frequently not equivalent when a simple conversion of units is made from one scale to another. In the case of weak complexes, discrepancies of this type are particularly important.

Activity coefficient effects have largely been ignored in applications of the B–H method. However, it is apparent that in the case of weak complexes such effects cannot be safely neglected.^{4,9,10} In typical studies of the electron donor–acceptor systems to be considered here, the total concentration of an acceptor (A) is kept constant and small compared to the concentration of the donor (D). In such systems, values of the activity and activity coefficient of the donor can be assumed to equal those obtained for the binary system donor plus solvent. However, two of the unknown activity coefficients (γ_A and γ_{DA}) cannot be obtained directly from experiments on binary systems. In the absence of direct information about these parameters, two types of assumption have ordinarily been made in treating data for complexing

systems: (a) the activity coefficient quotient, Γ , is taken to be constant on some concentration scale; or (b) corrections for variation of activity coefficients with concentration are made by using some theory of non-electrolyte solutions^{4,10} (usually solubility parameter theory¹¹). In a variation of the former assumption, Hanna and Rose⁷ have introduced experimental values of γ_D , while assuming that γ_{DA}/γ_A is constant with varying donor concentration. Recently, an attempt has been made to reconcile values of K obtained from the polyiodide solubility method¹² with those derived from conventional spectral methods by assuming that γ_A can be calculated from the equations of solubility parameter theory.⁹ However, none of the reported procedures for treating activity effects is very satisfactory, and to the present there has been no direct information about the variation of γ_{DA} or γ_A with donor concentration (in the ternary system solvent–donor–acceptor).

The present article considers the problem of relating values of K and ϵ obtained from B–H type equations expressed in terms of various concentration scales, criticizes methods which have been proposed for correcting for variations in one or more of the activity coefficients (γ_D , γ_A , γ_{DA}), and introduces a technique by which the dependence of γ_{DA} on donor concentration can be obtained uniquely. This latter method combines results of the polyiodide solubility method with those of the B–H spectral method.

Concentration Scale Dependence of K and ϵ

Although it is generally realized that K and ϵ values determined from the B–H equation on one concentration scale are frequently inconsistent with those based on another scale, there is some confusion in the literature regarding the reason for these discrepancies and the relation of these differences to activity effects. Apparently, many investigators are unaware that definite mathematical relations exist among the K 's and ϵ 's determined from B–H plots for a given set of data on

(1) Presented in part at the 165th National Meeting of the American Chemical Society, Dallas, Texas, April 8–13, 1973.

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

(3) R. Foster, "Organic Charge Transfer Complexes," Academic Press, New York, N. Y., 1969, Chapter 6.

(4) R. L. Scott, *Recl. Trav. Chim. Pays-Bas*, **75**, 787 (1956).

(5) P. J. Trotter and M. W. Hanna, *J. Amer. Chem. Soc.*, **88**, 3724 (1966).

(6) I. D. Kuntz, Jr., F. P. Gasparro, M. D. Johnson, Jr., and R. P. Taylor, *J. Amer. Chem. Soc.*, **90**, 4778 (1968).

(7) M. W. Hanna and D. G. Rose, *J. Amer. Chem. Soc.*, **94**, 2601 (1972).

(8) M. I. Foreman and R. Foster, *Recl. Trav. Chim. Pays-Bas*, **89**, 1149 (1970).

(9) S. D. Christian, J. D. Childs, and E. H. Lane, *J. Amer. Chem. Soc.*, **94**, 6861 (1972).

(10) R. S. Mulliken and W. B. Person, "Molecular Complexes: A Lecture and Reprint Volume," Wiley-Interscience, New York, N. Y., 1969.

(11) J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott, "Regular and Related Solutions," Van Nostrand-Reinhold, New York, N. Y., 1970.

(12) J. D. Childs, S. D. Christian, and J. Grundnes, *J. Amer. Chem. Soc.*, **94**, 5657 (1972).

different concentration scales. These relations have been summarized in the second section of the Appendix.

In a widely quoted paper concerning the concentration scale dependence of the B-H parameters, it is argued that such a dependence is evidence for the existence of solution nonideality and/or solvent competition effects.⁵ Actually, discrepancies among K and ϵ values determined on the different concentration scales provide no information about deviations from ideality or the failure of any of the assumptions which are required in deriving the B-H equation; instead, they are dictated by the definite relations among the concentration units. For weak complexes, values of ϵ determined using different concentration scales can differ widely (which makes no sense physically), and the respective K values can vary considerably from the relations among the concentration scales. In fact, in the case of very weak complexes, negative values of K and ϵ can be obtained. On the other hand, when K values are large, eqs. 19a-19d reduce to the expected (infinite dilution) relations among the concentration scales.

Modifications of the B-H Equations to Include Activity Coefficients

In pursuing the idea that "donor nonideality effects could be detected by observing a concentration scale dependence of the structural parameter determined for the complex," Hanna and Rose⁷ have employed donor activities, rather than concentrations, in treating nmr data (on molality and mole fraction bases) for the benzene-caffeine complex in CCl_4 . Thus, a B-H equation with donor activity substituted for concentration would have the form (see the table of symbols in the Appendix)

$$\frac{c_A^0}{A} = \frac{1}{(K_x^{\text{B-H}})'(\epsilon_x^{\text{B-H}})'(a_D^m)^0 M_S} + \frac{1}{(\epsilon_x^{\text{B-H}})'} \quad (1)$$

Hanna and Rose emphasize that use of donor activities in the B-H type plot removes the concentration scale dependence of the nmr shift of the complex and brings $(K_m^{\text{B-H}})'$ and $(K_x^{\text{B-H}})'$ into their proper relationship (*i.e.*, $K_m = K_x M_S/1000$). This result can be anticipated if one considers the simple relation between $(a_D^m)^0$ and $(a_D^x)^0$,¹³ *i.e.*

$$(a_D^x)^0 = (a_D^m)^0 M_S/1000 \quad (2)$$

(13) The activity of a species on one concentration scale must of course be proportional to its activity on all other concentration scales, at all concentrations. If infinitely dilute standard states are employed, the activity on each scale must approach the concentration on that scale at infinite dilution. For solute i in S, using concentration scales ζ and χ

$$\begin{aligned} a_i^\zeta &\propto a_i^\chi \\ a_i^\zeta/\zeta_i &\rightarrow 1 \text{ as } \zeta_i \rightarrow 0 \\ a_i^\chi/\chi_i &\rightarrow 1 \text{ as } \chi_i \rightarrow 0 \end{aligned}$$

or

$$\frac{a_i^\zeta}{a_i^\chi} = \lim_{\substack{\zeta_i \rightarrow 0 \\ \chi_i \rightarrow 0}} \left[\frac{\zeta_i}{\chi_i} \right]$$

Thus, the activities on two concentration scales are in the same ratio as the concentrations at infinite dilution, with proportionality constants depending only on properties of the pure solvent. For example, activities on molal and mole fraction bases will be related by $a_i^m = a_i^x M_S/1000$ at all concentrations. The activity coefficients will be related by $\gamma_i^m = \gamma_i^x x_S$.

Substitution of eq 2 into eq 1 (with $\zeta = x$) gives

$$\frac{c_A^0}{A} = \frac{1000}{(K_x^{\text{B-H}})'(\epsilon_x^{\text{B-H}})'(a_D^m)^0 M_S} + \frac{1}{(\epsilon_x^{\text{B-H}})'}$$

Comparison with eq 1 (with $\zeta = m$) shows that

$$(\epsilon_m^{\text{B-H}})' = (\epsilon_x^{\text{B-H}})'$$

and

$$(K_m^{\text{B-H}})' = (K_x^{\text{B-H}})' M_S/1000$$

Therefore, Hanna and Rose's findings are necessitated by the definite relations among activities on the different concentration scales. Furthermore, it can be shown that the interpretation of the K 's and ϵ 's derived using donor activities is subject to uncertainty for the same reason that the interpretation of the parameters derived from a normal B-H type plot is uncertain, namely that not all activity coefficients are taken into account.

If concentration dependent activity coefficients are introduced into the B-H type equations, relations can be developed between the thermodynamic K 's (*i.e.*, equilibrium constants expressed in terms of activities) and the K 's obtained from B-H type equations. Using the relation

$$K_\zeta^{\text{B-H}} = \frac{\zeta_{\text{DA}}}{\zeta_{\text{D}}\zeta_{\text{A}}} = \frac{(a_{\text{DA}}^\zeta/a_{\text{D}}^\zeta a_{\text{A}}^\zeta)}{(\gamma_{\text{DA}}^\zeta/\gamma_{\text{D}}^\zeta \gamma_{\text{A}}^\zeta)} = \frac{K_\zeta^{\text{th}}}{\Gamma_\zeta}$$

the B-H equation can be written

$$\frac{c_A^0}{A} = \frac{\Gamma_\zeta}{K_\zeta^{\text{th}} \epsilon_\zeta^{\text{B-H}} \zeta_{\text{D}}^0} + \frac{1}{\epsilon_\zeta^{\text{B-H}}}$$

If γ_i^ζ is expressed as

$$\gamma_i^\zeta = 1 + \nu_i^\zeta \zeta_{\text{D}}^0 + \beta_i^\zeta (\zeta_{\text{D}}^0)^2 + \dots \quad (3)$$

Γ_ζ becomes

$$\Gamma_\zeta = \frac{(1 + \nu_{\text{DA}}^\zeta \zeta_{\text{D}}^0 + \dots)}{(1 + \nu_{\text{D}}^\zeta \zeta_{\text{D}}^0 + \dots)(1 + \nu_{\text{A}}^\zeta \zeta_{\text{D}}^0 + \dots)} \quad (4)$$

Simplifying and retaining only first-order terms in ζ_{D}^0 (*i.e.*, assuming small $\nu_i^\zeta \zeta_{\text{D}}^0$) results in

$$\Gamma_\zeta = 1 + (\nu_{\text{DA}}^\zeta - \nu_{\text{D}}^\zeta - \nu_{\text{A}}^\zeta) \zeta_{\text{D}}^0 \quad (5)$$

Substituting this expression into eq 10 gives

$$\frac{c_A^0}{A} = \frac{1 + (\nu_{\text{DA}}^\zeta - \nu_{\text{D}}^\zeta - \nu_{\text{A}}^\zeta) \zeta_{\text{D}}^0}{K_\zeta^{\text{th}} \epsilon_\zeta^{\text{B-H}} \zeta_{\text{D}}^0} + \frac{1}{\epsilon_\zeta^{\text{B-H}}}$$

or

$$\frac{c_A^0}{A} = \frac{1}{K_\zeta^{\text{th}} \epsilon_\zeta^{\text{B-H}} \zeta_{\text{D}}^0} + \frac{1}{\epsilon_\zeta^{\text{B-H}}} \times \left[\frac{K_\zeta^{\text{th}} + (\nu_{\text{DA}}^\zeta - \nu_{\text{D}}^\zeta - \nu_{\text{A}}^\zeta)}{K_\zeta^{\text{th}}} \right] \quad (6)$$

so that $K_\zeta^{\text{B-H}}$ (intercept/slope) is related to K_ζ^{th} by

$$K_\zeta^{\text{B-H}} = K_\zeta^{\text{th}} + (\nu_{\text{DA}}^\zeta - \nu_{\text{D}}^\zeta - \nu_{\text{A}}^\zeta) \quad (7)$$

Replacing $(K_\zeta^{\text{B-H}})'$ by $K_\zeta^{\text{th}}(\gamma_{\text{A}}^\zeta/\gamma_{\text{DA}}^\zeta)$ in eq 1 (Hanna-Rose type equation);⁷ γ_{D}^ζ is included in the $(a_{\text{D}}^\zeta)^0$ term results in the following relation

$$\frac{c_A^0}{A} = \frac{\gamma_{\text{DA}}^\zeta/\gamma_{\text{A}}^\zeta}{K_\zeta^{\text{th}}(\epsilon_\zeta^{\text{B-H}})'(a_{\text{D}}^\zeta)^0} + \frac{1}{(\epsilon_\zeta^{\text{B-H}})'}$$

In a development analogous to that given in eq 3-7,

in which $\gamma_{DA}^{\zeta}/\gamma_A^{\zeta}$ is expressed as $\gamma_{DA}^{\zeta}/\gamma_A^{\zeta} = 1 + (\nu_{DA}^{\zeta} - \nu_A^{\zeta})(a_D^{\zeta})^0$, it can be shown that $(K_{\zeta}^{B-H})'$ is related to K_{ζ}^{th} by

$$(K_{\zeta}^{B-H})' = K_{\zeta}^{th} + (\nu_{DA}^{\zeta} - \nu_A^{\zeta}) \quad (8)$$

Equations 7 and 8 show that both K_{ζ}^{B-H} and $(K_{\zeta}^{B-H})'$ differ from the thermodynamic K by constants expressing activity coefficient dependence on concentration. Both types of equilibrium constant are ambiguous as long as activity coefficients are unknown. Since these correction terms (ν 's) can be expected to vary considerably from one complex to another, there appears to be no satisfactory general reason for preferring K and ϵ values derived by the method of Hanna and Rose to those obtained from one or another of the B-H type equations.

Utilization of Data from the Polyiodide Solubility Method to Obtain γ_{DA}

Recently, extensive results have been reported for aromatic donor-I₂ complexes in heptane, based on new spectral data and data obtained with the polyiodide solubility method.^{12,14} In obtaining the solubility results, mixtures of tetramethylammonium (TMA) polyiodides (here, TMAI₃ and TMAI₅) were employed to maintain a constant activity of iodine, and the total solubility of iodine was measured as a function of the concentration of added donor. If the effect of added donor on the activity coefficients of the solutes could be ignored, the solubility method would provide a very direct measure of the concentration of the complex, and hence K . In the absence of activity coefficient effects the total solubility of iodine at a given donor concentration would be

$$[A]_{c_D} = c_A + c_{DA} \quad (9)$$

Then, the increase in acceptor concentration which occurs as donor is added would simply be

$$[A]_{c_D} - [A]_{c_D=0} = c_{DA}$$

and the equilibrium constant would be given by

$$K = ([A]_{c_D} - [A]_{c_D=0})/([A]_{c_D=0}c_D)$$

However, a careful examination of the influence of activity coefficient effects makes it clear that K values derived from the solubility method are still not unambiguous, in spite of the fact that the data from which K is inferred can be restricted to concentration regions in which c_D , c_A , and c_{DA} are all extremely small. It can be shown that the solubility method will lead to the correct (thermodynamic) equilibrium constant only if γ_A^c is strictly constant throughout the range of donor concentrations employed.⁹ However, there are good theoretical reasons for believing that $d\gamma_A^c/dc_D \neq 0$, even in the limit of infinite dilution.¹¹ Therefore, one can anticipate that an activity coefficient correction term, similar to the final terms in eq 7 and 8, will appear in the expression which relates K^{sol} to K^{th} .

With the inclusion of activity coefficient terms eq 9 becomes

$$[A]_{c_D} = \frac{a_A^c}{\gamma_A^c} + \frac{a_{DA}^c}{\gamma_{DA}^c}$$

(14) J. D. Childs, Ph.D. Dissertation, The University of Oklahoma, 1971.

or

$$[A]_{c_D} = \frac{a_A^c}{\gamma_A^c} + \frac{K_{\zeta}^{th} a_A^c a_D^c}{\gamma_{DA}^c} \quad (10)$$

When the uncorrected solubility method is used, data obtained in regions of low donor concentration are fitted to the equation

$$[A]_{c_D} = a_A^c + K_{\zeta}^{sol} c_D a_A^c$$

Thus

$$K_{\zeta}^{sol} = \lim_{c_D \rightarrow 0} \left(\frac{1}{a_A^c} \frac{d[A]_{c_D}}{dc_D} \right) \quad (11)$$

where a_A^c , the constant activity of iodine, equals $[A]_{c_D=0}$. Equation 10 (with a_D^c replaced by $c_D \gamma_D^c$) may be differentiated with respect to c_D to yield

$$\frac{1}{a_A^c} \frac{d[A]_{c_D}}{dc_D} = \frac{d(1/\gamma_A^c)}{dc_D} + K_{\zeta}^{th} c_D \frac{d(\gamma_D^c/\gamma_{DA}^c)}{dc_D} + K_{\zeta}^{th} \left[\frac{\gamma_D^c}{\gamma_{DA}^c} \right] \quad (12)$$

Applying the limit $c_D \rightarrow 0$ to eq 12 and comparing with eq 11, one then obtains

$$K_{\zeta}^{sol} = K_{\zeta}^{th} - \nu_A^c \quad (13)$$

Note that $\lim_{c_D \rightarrow 0} \left[c_D \frac{d}{dc_D} \left(\frac{\gamma_D^c}{\gamma_{DA}^c} \right) \right] = 0$

$$\lim_{c_D \rightarrow 0} \left(\frac{\gamma_D^c}{\gamma_{DA}^c} \right) = 1$$

$$\lim_{c_D \rightarrow 0} \left[\frac{d(1/\gamma_A^c)}{dc_D} \right] = -\nu_A^c$$

Equation 13 shows how activity coefficient terms enter into the expression for K_{ζ}^{sol} ; it is analogous to eq 7 and 8 which relate K_{ζ}^{B-H} and $(K_{\zeta}^{B-H})'$ to K_{ζ}^{th} and the coefficients ν_{ζ}^{ζ} . K_{ζ}^{th} can be written in terms of the three types of equilibrium constants as

$$K_{\zeta}^{th} = K_{\zeta}^{sol} + \nu_A^{\zeta} \quad (14a)$$

$$K_{\zeta}^{th} = (K_{\zeta}^{B-H})' + (\nu_A^{\zeta} - \nu_{DA}^{\zeta}) \quad (14b)$$

$$K_{\zeta}^{th} = K_{\zeta}^{B-H} + (\nu_A^{\zeta} + \nu_D^{\zeta} - \nu_{DA}^{\zeta}) \quad (14c)$$

Equations 14a-c thus relate the various equilibrium constants, although K_{ζ}^{B-H} and $(K_{\zeta}^{B-H})'$ are obtained from the same data and are not independent (they differ by ν_D^{ζ} , which is explicitly accounted for in the Hanna-Rose method). However, it is interesting to consider the relation between K_{ζ}^{sol} and K_{ζ}^{B-H} .

$$K_{\zeta}^{sol} - K_{\zeta}^{B-H} = \nu_D^{\zeta} - \nu_{DA}^{\zeta} \quad (15)$$

Since K_{ζ}^{sol} and K_{ζ}^{B-H} are determined independently from solubility and spectral results, respectively, and since ν_D^{ζ} is measurable, eq 15 implies that ν_{DA}^{ζ} can be determined uniquely. The relation

$$\nu_{DA}^{\zeta} = \nu_D^{\zeta} - (K_{\zeta}^{sol} - K_{\zeta}^{B-H}) \quad (16)$$

can be applied to obtain γ_{DA}^{ζ} as a function of ζ_D for systems for which γ_D^{ζ} is known to linear terms in ζ_D .

Results and Discussion

Table I summarizes values of K_{ζ}^{sol} and K_{ζ}^{B-H} ob-

Table I. Equilibrium Constants for Complexes of Iodine with Aromatic Donors in Heptane at 25°^a

Donor	$K_c^{\text{sol}}, \text{l. mol}^{-1}$	$K_c^{\text{B-H}}, \text{l. mol}^{-1}$	$\Delta K (= \nu_D^c - \nu_{\text{DA}}^c)$
Benzene	0.36	0.20	0.16
Toluene	0.50	0.32	0.18
<i>o</i> -Xylene	0.64	0.42	0.22
<i>p</i> -Xylene	0.64	0.41	0.23
<i>m</i> -Xylene	0.70	0.54	0.16
Mesitylene	0.98	0.74	0.24

^a From ref 14.

tained in this laboratory for complexes of iodine with aromatic donors in heptane. The final column lists values of the difference between the two equilibrium constants, which by eq 15 is equal to $\nu_D^c - \nu_{\text{DA}}^c$ or

$$\lim_{c_D \rightarrow 0} \left[\frac{d}{dc_D} (\gamma_D^c - \gamma_{\text{DA}}^c) \right]$$

ν_D^c is known to be negative for all of these systems (since all deviate positively from Raoult's law); therefore, it can be seen that ν_{DA}^c is also negative for each complex and larger in magnitude than ν_D^c . Accurate values of ν_D^c are not presently available for all of the systems represented in Table I. However, reasonably precise values of activity coefficients have been determined for both components of the binary mixture benzene–heptane at 25°. The value of $\nu_{\text{C}_6\text{H}_6}^c$ is calculated to be -0.14 , using the data of Harris and Dunlop.¹⁵ Thus, from the value of $K_c^{\text{sol}} - K_c^{\text{B-H}}$ listed in Table I, $\nu_{\text{C}_6\text{H}_6-\text{I}_2}^c$ is calculated (via eq 16) to be $-0.16 - 0.14 = -0.30$. Similarly, from solubility parameter theory, $\nu_{\text{C}_6\text{H}_6}^c$ is estimated to be -0.15 , and from eq 16, the estimated value of $\nu_{\text{C}_6\text{H}_6-\text{I}_2}^c$ is -0.31 . Table II summarizes these

Table II. Thermodynamic Parameters for the Donor–Iodine–Heptane System at 25°

Donor	ν_D^c ^a	ν_{DA}^c ^b	ν_A^c ^a	$K_c^{\text{th}}, \text{l. mol}^{-1}$ ^d	α'
Benzene	-0.14^c	-0.30	-0.27	0.09	0.73
Benzene	-0.15	-0.31	-0.27	0.09	0.74
Toluene	-0.13	-0.31	-0.26	0.24	0.79
<i>o</i> -Xylene	-0.15	-0.37	-0.29	0.35	0.84
<i>p</i> -Xylene	-0.13	-0.35	-0.25	0.39	0.92
<i>m</i> -Xylene	-0.13	-0.29	-0.26	0.44	0.74
Mesitylene	-0.14	-0.38	-0.27	0.71	0.93

^a Equations of solubility parameter theory¹¹ were used to estimate these values, except where noted otherwise. ^b Calculated from ΔK values (Table I) and ν_D^c values. ^c Calculated from activity data in ref 15. ^d Due to an oversight, the thermodynamic (corrected) equilibrium constants given in ref 9 and 14 were slightly in error; the proper values (calculated from eq 14a) are given here.

calculated values, along with results for the other systems in Table I. Reliable activity data at 25° are not available for the other systems; therefore, solubility parameter theory has been applied to obtain ν_D^c values. In the case of the heptane–toluene system, value of γ_{toluene} are available in the temperature range 98–110°,¹⁶ and by using heat of solution data,¹⁷ it is possible to estimate

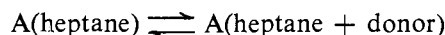
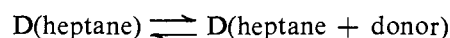
(15) K. R. Harris and P. J. Dunlop, *J. Chem. Thermodyn.*, **2**, 805 (1970).(16) H. Hipkin and H. S. Myers, *Ind. Eng. Chem.*, **46**, 2524 (1954).(17) H. W. Schnaible, H. C. van Ness, and J. M. Smith, *Amer. Inst. Chem. Eng. J.*, **3**, 147 (1957).

activity coefficients at 25°. These values agree well with the predictions of solubility parameter theory.

The values of ν_{DA}^c in Table II are of intrinsic interest, inasmuch as they represent the only information presently available about the effect of solvents on the activity coefficients of molecular complexes in the dilute solution region. Evidently the solvation of the aromatic donor–iodine complexes by the donor–heptane solvent mixtures is considerably greater than the solvation of the uncomplexed donor molecules. The observation that values of ν_{DA}^c are large negative numbers should serve as a warning that even in the submolar concentration range activity coefficient effects can significantly influence reported values of equilibrium constants and extinction coefficients.

If information were also available about ν_A^c , it would be possible to determine Γ_c experimentally and hence to calculate K_c^{th} . Unfortunately, we know of no way to determine experimental values of ν_A^c in the ternary systems heptane–donor–I₂; however, solubility parameter theory can again be used to estimate γ_A^c and ν_A^c . Column 3 in Table II includes calculated values of ν_A^c , and the next to the last column lists K_c^{th} values estimated for each complex, calculated from eq 14a. Note that for all of the aromatic donor system the equilibrium constants are in the following order: $K_c^{\text{sol}} > K_c^{\text{B-H}} > K_c^{\text{th}} > (K_c^{\text{B-H}})'$. There is no reason to expect that in general a K_c value derived by one technique will more nearly approximate K_c^{th} than will values obtained from other techniques, although for weak complexes the $\Delta\nu_i^c$ terms in the equations relating K_c^{th} to $K_c^{\text{B-H}}$ and $(K_c^{\text{B-H}})'$ (eq 14b and 14c) may frequently be approximately equal to zero. However, it has been argued that properties of the electronic spectral bands of the aromatic donor–iodine complexes inferred from the solubility results¹⁴ appear to be in better agreement with trends predicted from the Mulliken theory¹⁰ than are results inferred from the other methods.⁹

The estimated values of ν_i^c given in Table II (where $i = \text{D, A, or DA}$) can be used to determine the transfer free energy fraction, α' , for the complexing systems.¹⁸ Consider the three transfer reactions



For each of these steps, a solute species is transferred from the unit molarity ideal dilute solution state in heptane (S) into the corresponding ideal dilute solution state in a donor–heptane mixture (S + D). At any given concentration of donor, α' is given by

$$\alpha' = \frac{\Delta G_{\text{DA}}^{\circ}}{S \rightarrow (S+D)} / \left[\frac{\Delta G_{\text{D}}^{\circ}}{S \rightarrow (S+D)} + \frac{\Delta G_{\text{A}}^{\circ}}{S \rightarrow (S+D)} \right]$$

$$\alpha' = RT \ln \gamma_{\text{DA}}^c / (RT \ln \gamma_D^c + RT \ln \gamma_A^c) \quad (17)$$

But at sufficiently low donor concentration, each of the $\ln \gamma_i^c$ terms is equal to $\nu_i^c c_D$, so that eq 17 becomes

$$\alpha' = \nu_{\text{DA}}^c / (\nu_D^c + \nu_A^c) \quad (18)$$

(18) S. D. Christian, A. A. Taha, and B. W. Gash, *Quart. Rev.*, **24**, 20 (1970); S. D. Christian and E. H. Lane in "Solutions and Solubilities," M. R. J. Dack, Ed., Wiley-Interscience, New York, N. Y., in press. These articles include discussions of transfer free energy fractions and transfer energy fractions.

(Note that α' is independent of c_D in the concentration region in which only first-order terms in c_D are required in eq 3.) Values of α' , calculated from the ν_i^c values by using eq 18, are listed in the last column of Table II. α' is in each case in the range 0.70 to 0.95, which is typical for relatively weak molecular complexes.¹⁸ The magnitude of the solvation free energy or energy of a weak complex is ordinarily somewhat less than that of the separated donor plus acceptor molecules, presumably because formation of the complex renders a fraction of the molecular surface of the reactive groups of the monomer inaccessible to contact with solvent. There seems to be a tendency for the α' values in Table II to increase as the donor strength increases, although the *m*-xylene results do not follow this trend.

An independent estimate of α' can be made for the benzene-I₂ complex, for which K_c values are available for both the gas phase and heptane solution. From solubility and activity data,^{15,19} the transfer free energies of I₂ and benzene (from the unit molarity ideal gaseous states into the unit molarity ideal dilute solution in heptane) are determined to be -4.6 and -4.0 kcal, respectively. Using these values together with a K_c value of 4.0 l. mol⁻¹ in the gas phase²⁰ and the K_c^{th} value in heptane (0.09 l. mol⁻¹), one can calculate that the transfer free energy of benzene-I₂ is -6.4 kcal. Thus, $\alpha' = 6.4/(4.0 + 4.6) = 0.74$; this value is fortuitously close to the values in Table II (0.73 and 0.74). Similar estimates of α' cannot be made for the other systems because gas phase K_c values are lacking.

Summary

The present article details the difficulties which are inherent in methods which have been applied to investigate weak molecular complexes in solution. It is shown that neither the Benesi-Hildebrand method (or its modifications) nor the uncorrected solubility method leads directly to values of the thermodynamic equilibrium constant. Expressions have been given to interrelate K and ϵ values based on the various concentration scales and to indicate explicitly how activity coefficient correction terms enter to complicate the interpretation of K values determined by the various methods (*viz.*, the Benesi-Hildebrand, Hanna-Rose, and polyiodide solubility methods). A combination of solubility and B-H results is shown to lead to unambiguous values of activity coefficients of aromatic donor-iodine complexes. Use of the solubility parameter theory, along with derived expressions involving activity coefficients, yields values of the transfer free energy fraction (α') which are in the range 0.70-0.95 for the aromatic donor-I₂ complexes.

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(20) This value is intermediate between the equilibrium constants determined for C₆H₆-I₂ at 25° in the gas phase by F. T. Lang and R. L. Strong, *J. Amer. Chem. Soc.*, **87**, 2345 (1965) ($K_c = 4.5$ l. mol⁻¹) and D. Atack and O. K. Rice, *J. Phys. Chem.*, **58**, 1017 (1954) ($K_c = 3.4$ l. mol⁻¹).

Appendix

A. Benesi-Hildebrand Type Equations. The Benesi-Hildebrand (B-H) equation² is written as

$$\frac{c_A^0}{A} = \frac{1}{K_{\zeta}^{\text{B-H}} \epsilon_{\zeta}^{\text{B-H}} \zeta_D^0} + \frac{1}{\epsilon_{\zeta}^{\text{B-H}}}$$

where ζ represents a concentration scale label ($\zeta = c, m, x, \text{ or } r$). One assumes that $c_D^0 \gg c_A^0$ and that corrections have been made for absorbance by the uncomplexed donor and acceptor.

The Scatchard equation²¹

$$\frac{A}{c_A^0 \zeta_D^0} = K_{\zeta} \epsilon_{\zeta} - \frac{K_{\zeta} A}{c_A^0}$$

is used in some of the articles mentioned above. The conclusions made regarding the B-H equation also hold for the Scatchard equation, for other related equations,³ and for analogous forms in use with nonoptical studies³ (these equations are all referred to here as B-H type equations).

B. Relations among $K^{\text{B-H}}$ and $\epsilon^{\text{B-H}}$ Values on Different Concentration Scales. One can derive mathematical relations among K 's and ϵ 's determined from B-H type plots for a given set of data on different concentration scales. The equations are developed by relating the total donor concentration on the different concentration scales (assuming ideal volume of mixing and that $c_D^0 \gg c_A^0$) and by substituting these relations into B-H type equations. The appropriate slopes and intercepts are then equated to give the following relations.²²

$$K_c^{\text{B-H}} = \bar{V}_s K_x^{\text{B-H}} + (\bar{V}_s - \bar{V}_D)$$

$$\epsilon_c^{\text{B-H}} = \epsilon_x^{\text{B-H}} \left[\frac{K_x^{\text{B-H}} \bar{V}_s}{K_x^{\text{B-H}} \bar{V}_s + (\bar{V}_s - \bar{V}_D)} \right] \quad (19a)$$

$$K_m^{\text{B-H}} = (K_x^{\text{B-H}} + 1) M_s / 1000$$

$$\epsilon_m^{\text{B-H}} = \epsilon_x^{\text{B-H}} \left(\frac{K_x^{\text{B-H}}}{K_x^{\text{B-H}} + 1} \right) \quad (19b)$$

$$K_c^{\text{B-H}} = (K_m^{\text{B-H}} / \rho_s) - \bar{V}_D$$

$$\epsilon_c^{\text{B-H}} = \epsilon_m^{\text{B-H}} \left(\frac{K_m^{\text{B-H}}}{K_m^{\text{B-H}} - \rho_s \bar{V}_D} \right) \quad (19c)$$

$$K_r^{\text{B-H}} = K_x^{\text{B-H}} + (M_D / 1000)$$

$$\epsilon_r^{\text{B-H}} = \epsilon_x^{\text{B-H}} \left[\frac{K_x^{\text{B-H}}}{K_x^{\text{B-H}} + (M_D / 1000)} \right] \quad (19d)$$

C. Table of Symbols

ζ_i	concentration of the <i>i</i> th species ($\zeta = c, m, x, \text{ or } r$); a zero superscript indicates total (analytical) concentration
<i>c</i>	concentration in moles/liter (molarity)
<i>m</i>	concentration in moles/kilogram of solvent (molality)
<i>x</i>	concentration in mole fraction
<i>r</i>	concentration in moles/kilogram of solution
D	donor
A	acceptor
DA	complex
S	solvent
A	absorbance per unit path length

(21) G. Scatchard, *Ann. N. Y. Acad. Sci.*, **51**, 660 (1949).

(22) Equations 19a and 19c have been reported previously.^{6,23}

(23) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964.

$K_{\zeta}^{\text{B-H}}$	formation constant derived from a B-H type plot using the ζ concentration scale	γ_i	activity coefficient of the i th species on the ζ concentration scale
$(K_{\zeta}^{\text{B-H}})'$	formation constant derived from a B-H type plot with $(a_{\text{D}}^{\zeta})^0$ substituted for ζ_{D}^0	Γ_{ζ}	$\gamma_{\text{DA}}^{\zeta}/\gamma_{\text{D}}^{\zeta}\gamma_{\text{A}}^{\zeta}$
$\epsilon_{\zeta}^{\text{B-H}}$	complex absorptivity from same plot as $K_{\zeta}^{\text{B-H}}$	K_{ζ}^{th}	$a_{\text{DA}}^{\zeta}/a_{\text{D}}^{\zeta}a_{\text{A}}^{\zeta}$
$(\epsilon_{\zeta}^{\text{B-H}})'$	complex absorptivity from same plot as $(K_{\zeta}^{\text{B-H}})'$	ν_i^{ζ}	$\lim_{\zeta_{\text{D}}^0 \rightarrow 0} d\gamma_i^{\zeta}/d\zeta_{\text{D}}^0$
\bar{V}_i	molar volume of the i th species (in liters)	$[\text{A}]_{\text{cD}}$	total I_2 solubility at a donor concentration c_{D} (in the polyiodide solubility method ¹²)
M_i	molecular weight of the i th species	K_{ζ}^{sol}	formation constant from the solubility method
ρ_i	density of the i th species (in grams/milliliter)	$\Delta G_i^{\circ} \text{S} \rightarrow (\text{S} + \text{D})$	standard free energy of transfer for the i th species from S to S + D
a_i^{ζ}	activity of the i th species on the ζ concentration scale		
$(a_i^{\zeta})^0$	a_i^{ζ} corresponding to ζ_{D}^0		

Structure of the Cubic Phase of Xenon Hexafluoride at 193°K

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Abstract: The structure of the cubic phase of XeF_6 was determined by X-ray diffraction at 193°K. The cell constant is 25.06 Å, space group symmetry $Fm\bar{3}c$, with 144 XeF_6 per unit cell. The structure is not molecular but based on the association of XeF_5^+ and F^- ions into tetrameric and hexameric rings. The structure is disordered and the 1008 atoms in the cell are distributed over 1600 positions. The polymeric rings are three dimensional in nature and achieve a nearly spherical overall shape. This permits the positive and negative charges to be distributed over concentric spherical shells. The shape of the XeF_5^+ ion is in accord with the expectations of the Gillespie-Nyholm valence-shell electron pair repulsion theory.

Xenon hexafluoride is polymorphic and exists in four phases.² Studies of the heat capacity and other thermodynamic functions³ indicate that phase I is stable from the melting point (322.63°K) to about 291.8°K, where it is transformed to phase II, in turn stable to about 253.8°K, below which phase III exists. Phase IV which is cubic is stable from the melting point of $\sim 301^\circ\text{K}$ down to at least 93°K.² Phase I was identified as monoclinic with eight XeF_6 units in the cell by Agron, *et al.*⁴ The structural basis underlying phases I, II, and III^{5,6} did not become clear until the structure of phase IV was determined.⁷ Phases I, II, and III are based on the association of XeF_5^+ and F^- ions into tetrameric rings. Phase I is monoclinic with 2 tetramers per cell, phase II is orthorhombic with 4 tetramers per cell, and phase III is monoclinic with 16 tetramers per cell.⁶ The $\text{I} \rightleftharpoons \text{II}$ and $\text{II} \rightleftharpoons \text{III}$ transformations are interpretable in terms of various degrees of ordering of a common underlying tetrameric unit.

Phase IV was first observed (but not so designated) by Agron, *et al.*⁴ They reported a large cubic unit cell with $a = 25.34$ Å (temperature not specified but presumably room temperature) and probable space group $F\bar{4}3c$ or $Fm\bar{3}c$.

The varying degrees of disorder plus low symmetry present in phases I, II, and III make it unlikely that a

detailed structural description will be forthcoming for any one of these phases. Hence, it appears desirable to present more information on the analysis of phase IV than was included in the earlier communication.⁷

Experimental Section

The sodium fluoride complexing method was used to prepare and purify XeF_6 .^{3b} Capillaries of FEP (fluorinated ethylene propylene copolymer) were prefluorinated with XeF_6 and heat sealed after introduction of the specimens. Well-formed crystals of cubic XeF_6 invariably resulted when capillaries of FEP partly filled with XeF_6 were maintained at 291°K for several days.

The X-ray system was comprised of a precession camera, a manually operated single crystal orienter mounted on a G.E. XRD-5 diffractometer, cooling facilities, and a means for transferring a specimen from precession camera to diffractometer under low-temperature conditions. The precession camera was fitted with a polarizing microscope and means for optical illumination. The cooling system was an improved version of one used in studying interhalogen compounds.⁸ Details of the cryostat will appear elsewhere.⁹

A crystal with dimensions of $1 \times 0.5 \times 0.2$ mm was used for intensity measurements. $\text{Mo K}\alpha$ radiation, $\lambda 0.7107$ Å, was used for both photographic and counting measurements. As the temperature is lowered, the X-ray reflections become increasingly stronger, but it also becomes progressively more difficult to avoid frost formation when the specimen is on the diffractometer. A temperature of 193°K was selected as a compromise between the quality of data and experimental difficulties. A scintillation counter was used with the stationary crystal technique. Ten-second counts at peak and at background on both sides of each reflection were made. Counting rates were kept below 10,000 per second by the use of Zr attenuators of known absorption. The crystal was mounted with the [011] direction parallel to the φ axis of the diffractometer. The absorption error was obtained empirically by measuring $0hh$ reflections at $\chi = 90^\circ$ through a 360° range in φ . The intensities varied by 65% from minimum to maximum transmission. The unique reflections out to $2\theta = 60^\circ$ numbered 1023. They were measured in the sector

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