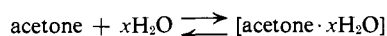


of the ion-pair formation process with H-bonding processes in the mixed solvent. Andreae and co-workers¹⁹ have shown the necessity of considering the process



and have been able to deduce tentative values of x and K_{eq} for such processes. This chemical formulation of solvent mixture nonideality lacks the formal elegance of the more physical approaches yet promises to add greatly to our chances of solving the solvent-dependence problem.

Figure 2 shows the Walden product for the systems examined. The Walden product behaves in an ideal fashion for both salts in the low organic range, then starts decreasing drastically. Thus even a system that exhibits apparent ideal behavior for K_A need not exhibit ideality in its hydrodynamic parameters.

Acknowledgments. The authors acknowledge the support of the United States Atomic Energy Com-

(19) See J. Lamb, "Dispersione ed Assorbimento del Suono nei Processi Molecolari," Academic Press, Inc., New York, N. Y., 1963, p. 101.

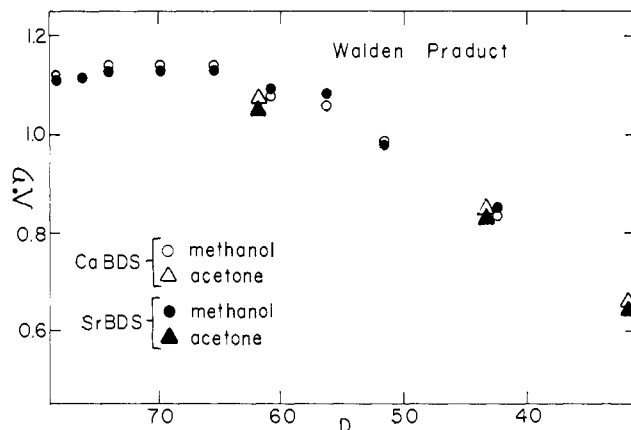


Figure 2.

mission under Contract AT-[40-1]-2983 during the course of this research. They would also like to express their appreciation to Mr. Bert R. Staples and Mr. David W. Ebdon for their aid in the computer calculations.

A Criterion for Reliability of Formation Constants of Weak Complexes

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A critical examination of the use of the Benesi-Hildebrand or Scott equations to obtain K and ϵ for weak complexes emphasizes the obvious: namely, the most accurate values for formation constants of a complex are obtained when the equilibrium concentration of the complex is of the same order of magnitude as the equilibrium concentration of the more dilute component. For complexes measured by the Benesi-Hildebrand method or one of its many variations, this condition requires that the donor concentration in the most concentrated solution must be greater than about $0.1(1/K)$. If it is less than this value, then the Benesi-Hildebrand plot will give zero intercept, and the Scott plot will give zero slope, within the experimental error, even though K may be moderately large and ϵ is finite. An examination of a few examples, selected at random from the literature, illustrates the application of this criterion to weak complexes for which experimental conditions are such that they either fail or just barely satisfy the criterion, suggesting strongly that the reported values of K are not significant.

Introduction

Although a healthy skepticism regarding the existence of weak complexes existed in the early years of the history of electron donor-acceptor complexes, the tendency in recent years has been to accept their existence

much more readily. In fact there are now several examples in the literature of complexes for which the experimental evidence for their existence leaves much to be desired. Certainly, if there were not a good reason from theory to expect a complex between anthracene and iodine, we should hate to accept evidence such as that presented recently¹ as proof that the complex really exists.

This remark applies with equal force to a number of other recent reports of "complex formation." To single out just one other paper, we may consider the report of complex formation between CCl_4 and aromatic donors.² In view of the importance of the question of existence of some of these interesting complexes, and in view of the number of studies of these difficult borderline cases, it would seem desirable to analyze critically the method of study, in order to determine its reliability.

The existence of the complex is deduced from the analysis of some change in the absorption spectrum of the mixture when compared to the spectrum of the individual components. From a study of these changes as a function of the concentration of the components, the values of the equilibrium constant K and molar absorptivity ϵ can be determined separately. Some

(1) J. Peters and W. B. Person, *J. Am. Chem. Soc.*, **86**, 10 (1964).

(2) R. Anderson and J. M. Prausnitz, *J. Chem. Phys.*, **39**, 1225 (1963).

modification of the Benesi-Hildebrand procedure³ is almost always used. Perhaps the most common form is the Scott modification.⁴ Other modifications, such as those attributed to Ketelaar,⁵ Rose and Drago,⁶ and many others,⁷ which are based upon spectrophotometric procedures, are not basically different. It should be noted that the criterion for the existence of a complex is not the appearance of a new (or shifted) absorption band, but rather that the new absorption can be analyzed by one of the procedures above to give a single, nonzero, value for K and a finite, constant value for ϵ .

There have been several attempts recently to discuss this procedure critically.⁸⁻¹⁰ All these authors have emphasized the importance of including a discussion of experimental errors in the presentation of data. To this suggestion, this author can only add a fervent second. However, it would seem worthwhile to remind ourselves of the basic reason for difficulty with these weak complexes. Namely, reliable equilibrium constants are obtained only when the equilibrium concentration of the complex is of the same order of magnitude as the equilibrium concentration of the most dilute component. Let us now consider briefly the procedure for determining K and ϵ using the Scott equation, in order to understand more fully this difficulty.

Determination of K and ϵ

The procedure for determining the properties of the complex from spectrophotometric measurements consists of measuring the absorbance of the complex as a function of changing concentration of one of the components of the complex, and then plotting the data according to the Scott equation.⁴

$$\frac{[D][A]}{D_k} = \frac{1}{K\epsilon} + \frac{1}{\epsilon}[D] \quad (1)$$

Here $[D]$ and $[A]$ are the initial concentrations of the electron donor and acceptor, respectively; l is the path length; D_k is the absorbance at λ_k due only to the complex; K is the formation constant in l./mole (if the concentrations are in moles/l.); and ϵ is the molar absorptivity at λ_k . For the equation in this form, the concentration of the donor is much greater than the concentration of the acceptor. This condition is not important since the equation can be modified readily if acceptor is in excess, or if both concentrations are equal, but it often corresponds to practical considerations of solubility.

By measuring D_k for solutions with differing values of $[D]$ and plotting the data as in eq. 1, we obtain a straight line with intercept $1/K\epsilon$ and slope $1/\epsilon$; hence, we can determine K and ϵ separately, at least in principle.

For weak complexes, the difficulty comes in that it is not possible experimentally to obtain concentrations of complex high enough that the points plotted as the left-hand side of eq. 1 vs. $[D]$ become significantly different

from the intercept. This difficulty has been mentioned by Briegleb,¹¹ but apparently it should be re-emphasized. In fact, this difficulty is to blame for the problem of proving the existence of weak complexes.

In order to make clear the nature of this difficulty, let us consider how the absorbance varies as a result of increasing initial donor concentration, $[D]$, in this experiment. If the donor and acceptor form only a 1:1



complex, X , the absorbance D_k , is given by

$$D_k = \epsilon l[X] = \epsilon lK[D_{eq}][A_{eq}]$$

If $[D] \gg [A]$, then $[D_{eq}] \cong [D]$, the initial donor concentration, and $[A_{eq}] \cong [A] - [X]$. Now, if the concentration of donor is not high enough, then the concentration of complex in solution will be very small so that $[A_{eq}] \cong [A]$. In that case, $D_k \cong \epsilon lK[D][A]$ and the absorbance, D_k , increases linearly with increasing initial donor concentration. On the other hand, when the concentration of donor is such that all the acceptor is complexed, then further addition of donor does not change the absorbance. This behavior is shown in Figure 1.

We see in Figure 1 that the plot of absorbance vs. concentration of donor for this example can be divided into three regions. In the region of low donor concentration, the increase in absorbance with increasing $[D]$ is linear. In the region of high donor concentration, the absorbance does not change as $[D]$ increases. In between these extremes, there is a region in which the absorbance changes in a nonlinear manner as $[D]$ increases. It will be possible to obtain both K and ϵ from the spectrophotometric measurement *only* in the intermediate concentration range; this range is defined by: $0.1[A] < [X_{eq}] < 0.9[A]$, approximately. Since $[X] = K[D][A_{eq}]$, the concentration of $[X]$ is equal to $0.1[A]$ when $D = 0.1(1/K)$, and 90% complete complexation occurs when $[D]$ becomes greater than $9.0(1/K)$.

If we should try to analyze data which fall within region I of Figure 1 by the Scott equation, we should find that the points representing the left-hand side of eq. 1 fit a straight line with intercept = $1/K\epsilon$, but with zero slope, within experimental error. In region III, the points would fit a straight line with a slope of $1/\epsilon$, but with zero intercept.

Of course, the values of 0.1 and $9.0(1/K)$ defining region II are rather arbitrary limits, and it may be possible to push beyond them in certain cases. In order to investigate this question, let us consider the experimental scatter in the data used with eq. 1. If there were no scatter, then there would be no reason not to extend the limits of $[D]$ much further.

For this discussion, let us make the usual simplifying assumption that the relative error in the concentrations of $[D]$ and $[A]$ is much smaller than the relative error in D_k . This assumption is certainly not valid for all data in the literature, but it can be made true by careful experimental work; it is discussed elsewhere.⁷⁻⁹ The error in D_k will be of the order of ± 0.005 unit. The magnitude of D_k may be about 0.5, although it may range from about 0.1 to more than 1.0. (The experiment is designed to produce a value of the absorbance

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

(4) R. L. Scott, *Rec. trav. chim.*, **75**, 787 (1956).

(5) J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit, and W. Dzubas, *ibid.*, **71**, 1104 (1952).

(6) N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81**, 6138 (1959).

(7) See G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe" Springer-Verlag, Berlin, 1961.

(8) P. R. Hammond, *J. Chem. Soc.*, 479 (1964).

(9) K. Conrow, G. D. Johnson, and R. E. Bowen, *J. Am. Chem. Soc.*, **86**, 1025 (1964).

(10) S. Tamres, *J. Phys. Chem.*, **65**, 654 (1961).

(11) See ref. 7, p. 203.

in this range, either by adjusting l or $[D]$ and $[A]$.) Thus, the percentage error in the left-hand side of eq. 1 is about $\pm 1\%$.

Consider now the point at the highest initial donor concentration, $[D_m]$, in the plot of eq. 1. We must ask whether the ordinate of this point differs significantly from the intercept $(1/K\epsilon)$, so that the slope of the line determined from these points differs significantly from zero. At the 99% confidence level, two values differ from each other if the difference between them is greater than three times the standard deviation in the point. Thus, with a standard deviation of 1%, the ordinate of the point associated with $[D_m]$ should differ from $1/K\epsilon$ by more than $0.03(1/K\epsilon)$. Substitution into eq. 1 shows that this requires that $[D_m]$ be greater than $0.03(1/K)$.

Since our analysis (the use of three standard deviations at the 99% confidence level) assumes that the ordinate of the point associated with $[D_m]$ is determined as the mean of many measurements, whereas it is usually obtained from only a few, it seems that the lower limit for $[D_m]$ of $0.1(1/K)$ is a reasonable requirement.

We note that this rule is independent of the value of ϵ for the complex. We note also that it is not sufficient to require that the absorbance of the complex be large. High absorbance can occur even when the donor concentration is less than $0.03(1/K)$, but the absorbance will depend linearly (within experimental error) on $[D]$ and so K cannot be evaluated.

It is reasonable to ask at this point why a least-squares analysis of the data according to eq. 1 does not indicate trouble in the form of large standard deviations in K and ϵ . We believe it does, provided that one remembers that only ΔK values greater than three times the standard deviation are significant. Also, the concept of the sharpness of fit as used by Conrow, Johnson, and Bowen⁹ seems definitely useful. These ideas are illustrated in the next section. We might note here only that papers providing enough information to compute a standard deviation, or those which give standard deviations, are distressingly far apart.

Application of the Criterion

The rule that $[D_m]$ must be between 0.1 and 9.0 times the value of $(1/K)$ in order to evaluate K and ϵ separately from spectrophotometric measurements by eq. 1 imposes a lower limit on values of K which can be obtained reliably. For most organic liquids, the concentration of $[D_m]$, when used as pure solvent, is about $10 M$. Thus, values of K less than about 0.01 cannot be determined by this procedure, and reported values less than this value must be treated with suspicion.

On the other hand, for a good many systems the electron donor is not a liquid and may also have limited solubility, so that the practical limitation on the lowest values of K which can be determined may well be considerably higher than 0.01. Thus, the solubility of anthracene in CCl_4 is approximately $0.05 M$; hence, K must be greater than about 2 in order for it to be determinable by the spectroscopic procedure. Certainly the difficulties reported earlier¹ are understandable in terms of this analysis. The value of K is reported to be 3.7 ± 1.0 for the anthracene-iodine complex in CCl_4 and 2.4 ± 1.0 in CH_2Cl_2 . We must conclude, both from the

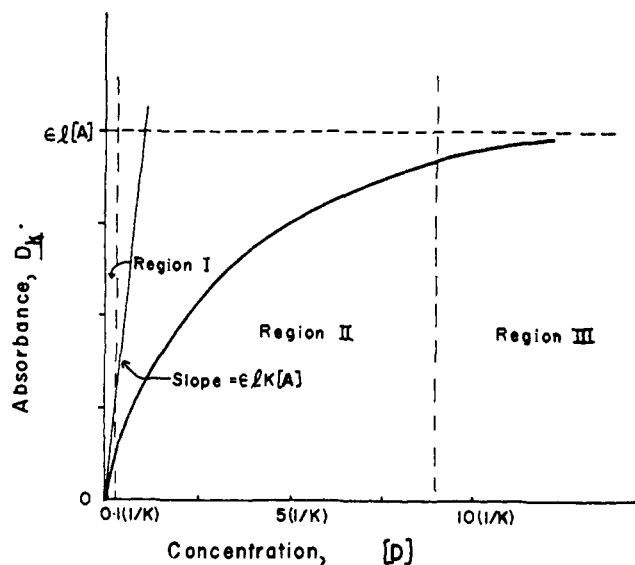


Figure 1. Variation of absorbance of the complex, D_k , as a function of increasing concentration of donor (donor in excess).

criterion that $[D_m] > 0.1(1/K)$ and from the criterion that ΔK be greater than three times the standard deviation, that the existence of the anthracene-iodine complex ($K > 0$) is only just barely proved.

The data for the complex between phenanthrene and iodine,¹ however, were obtained with donor concentrations up to $0.8 M$. Since K was reported to be 0.45 ± 0.06 , the data obtained from solutions with donor concentrations of 0.1 to $0.8 M$ should have been sufficient to determine a fairly accurate value of K , as we see from either criterion. On the other hand, Bhattacharya and Basu¹² attempted to obtain K for this complex from studies of solutions in which the phenanthrene concentration was $0.1 M$ or less. Apparently, this is the explanation for the difference between their results and those we reported.¹ Certainly the low concentrations used¹² must account for the very poor sharpness of fit found by Conrow, Johnson, and Bowen⁹ upon recomputing K from these¹² data.

To examine another system, we might consider the results reported by Anderson and Prausnitz² for the "complexes" between CCl_4 and aromatic hydrocarbons. They report values of K for benzene-carbon tetrachloride and mesitylene-carbon tetrachloride to be 0.009 ± 0.004 and 0.113 ± 0.044 , respectively. Their measurements were made with excess CCl_4 , in concentration up to $1.24 M$. Although they did not use the Scott equation to analyze their data, their procedure is not basically different. Hence, it seems quite unlikely that the values of K which they report for these complexes are significantly different from zero. This conclusion follows from the criterion on ΔK and also from the rule that the maximum acceptor concentration (excess acceptor) must be greater than $0.1(1/K)$. According to the latter rule, the minimum K which could be determined in this study is about 0.08.

Examination of the data summarized for iodine complexes in Briegleb⁷ (Tabelle 60) reveals several weak complexes with K values of the order of 0.01; namely, complexes of I_2 with tetrachloroethylene,¹³ cyclohex-

(12) R. Bhattacharya and S. Basu, *Trans. Faraday Soc.*, **54**, 1286 (1958).

(13) J. A. A. Ketelaar, *J. phys. radium*, **15**, 197 (1954).

ane,¹⁴ and dimethylbutane.¹⁴ It seems unlikely that these values of K are significant. Other values in that table are probably large enough to be significant, although one should examine the original references to find the donor concentrations used in obtaining K for the weaker complexes. It is worth noting parenthetically that such detailed experimental information is not always easy to find in the literature.

Contact Charge-Transfer Pairs

From our discussion above, it is obvious that the concept of contact charge-transfer pairs¹⁵ is connected with our analysis. Indeed, the experimental characteristic of contact charge-transfer pairs is an absorption band whose intensity is linearly dependent upon the initial concentration of the donor, to give a Scott plot with zero slope, as in the treatment above, or a Benesi-Hildebrand plot with zero intercept. From our analysis above, we see that such a plot can occur even for relatively strong complexes if the donor concentration is too low owing to poor choice of experimental conditions or limited solubility. It seems quite likely that the anthracene-iodine complex, for example, exists as a definite 1:1 complex, rather than as a weaker contact interaction, even though the experimental behavior of solutions at practical concentrations is identical with that for contact charge transfer.

The key question in attempts to distinguish between true complexes and contacts appears to be the question of whether the charge-transfer stabilization energy (which is greater than the ordinary van der Waals attraction energy) is greater than the translational kinetic energy of kT (or RT per mole). If it is, then we should consider the interaction to be best described as a "complex," stabilized by charge-transfer forces. If the energy of formation is less than kT , then the interaction is best described as a "contact," which may exhibit a charge-transfer absorption band. If the energy of formation is small, we should inquire as to whether it is

(14) S. H. Hastings, J. L. Franklin, J. C. Schiller, and F. A. Matsen, *J. Am. Chem. Soc.*, **75**, 2900 (1953).

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

due to an electrostatic energy greater between D and A than between D-D and A-A, or whether it is really due to the charge-transfer interaction. These questions are difficult, if not impossible, to answer.

Conclusion

The major conclusion which can be stated is that experimental error is important, and its effect on K and ϵ should be analyzed. This may seem obvious, but when one considers the amount of discussion in the literature of electron donor-acceptor complexes based upon erroneous data, or the discussion of discrepancies, such as "different" values of K in different solvents, which may agree well within the experimental error, then it does seem worthwhile emphasizing this conclusion. Perhaps further criteria for testing the reliability of the experimental data for these complexes may be stated which would permit critical use of the extensive data in the literature.

It should be noted that there are probably few data on donor-acceptor complexes in the literature which can survive the rigorous test on ΔK ($\Delta K > 3$ standard deviations). Failure does not necessarily mean that the complexes do not really exist or that their equilibrium constants are drastically different from the reported values. It just means that skepticism is warranted.

Finally, we note the danger in tabulating data from different complexes for comparison purposes when such tabulation separates K and ϵ . Because the use of eq. 1 gives $1/K\epsilon$ as the intercept, the experiment may well determine the product of $K\epsilon$ accurately, but the separation into K and ϵ individually may be seriously in error.

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Argentation Equilibria of Substituted Styrenes

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Contribution from the Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto, Japan. Received August 3, 1964

The equilibrium constants for the formation of silver ion complexes of various styrene derivatives in water have been determined at 25°. It is found that the equilibrium leading to the formation of 1:1 silver ion complexes of para- and meta-substituted styrenes obeys the Hammett relation with the reaction constant $\rho = -0.766$. The temperature dependence of the equilibrium has also been examined for styrene and its p-methyl and p-chloro derivatives. Analysis of the thermodynamic data obtained indicates that, in the ordinary temperature region,

the substituent effects are entropy controlled. A possible aspect of the origin of the Hammett relation observed is presented.

Introduction

It has been well demonstrated that transition meta cations such as Ag^+ , Cu^+ , and Hg^{2+} form coordination complexes with unsaturated compounds.^{1,2} In par-

(1) R. N. Keller, *Chem. Rev.*, **28**, 229 (1941).