A Statistical Assessment of Association Constants †

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A non-linear least-squares computation of association constants derived spectrophotometrically has been made. The calculation yields the equally important quantity, the error in the fitted parameter. New measurements on carbon tetrachloride complexes with benzene and with methyl-substituted benzenes are presented.

APPROXIMATE methods for fitting association constants, from absorbance data for example, are widely used. The method of Benesi and Hildebrand [1] is perhaps the best known. However, the combined effects of approximations and experimental error can introduce unnecessary faults into the fitted parameters. This had led one reviewer [2] to the perhaps rather too pessimistic view that possibly half the association constants ever reported are valueless. Such errors can be avoided by choosing parameters which minimise the quantity $\sum^{n}$-(calculated 'datum' — observed datum)[2] in an ordinary least-squares procedure. The calculated datum is calculated from the relevant functions (Beer's law and the mass action law without approximation) by use of successive estimates of the required parameters. The summation is taken over all n sets of observations, where each set is a pair of stoicheiometric concentrations and the absorbance of the solution. The usual Newton–Raphson method [3] is used to obtain successively better estimates of the parameters from the data, as outlined later. We gain the additional advantage of being able to make an objective statistical estimate of the errors in the parameters fitted which arise from the scatter in the measurements. In view of the opinion just cited,[2] clearly the establishment of the possible magnitude of the error in the parameter is as important as the establishment of a value for the parameter itself.

Since the start of our studies several publications on the topic have appeared. That by Wentworth,[4] based on the book by Deming [3] which we ourselves have followed, gives the most detailed exposition of the full statistical method for the fitting of association constants.

We thus report here only the results of using the method for obtaining association constants from literature data and from our own measurements, and treat the computational method only briefly. We also compare our
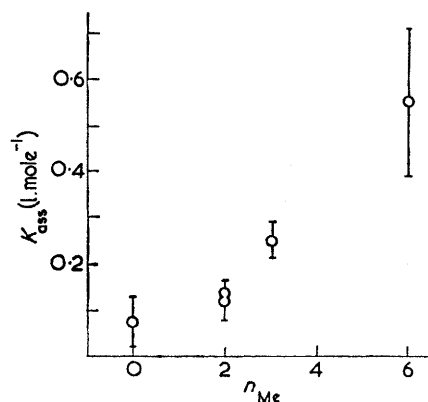

FIGURE 1   Sequence of K_{ass} values for complexes of benzene, and methylsubstituted benzenes, with carbon tetrachloride, *vs.* number of methyl substituents.

computational conclusions with those of some other workers.[4,5]

Our examination was prompted by an interest in the complexes formed between carbon tetrachloride and benzene or the methyl-substituted benzenes. Our measurements are given here for comparison with literature values.[6-8]

Outline of the Method of Least Squares.[3,4]   We determine here the *dissociation* constant K, for some algebraic convenience: $K = K_{ass}^{-1}$.

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For the system $A + B \rightleftharpoons X$, in equilibrium (where the concentrations of the three species are $a - x$, $b - x$ and x respectively) absorbances A depend on the extinction coefficient, ε, of X, and on x and therefore on K, a, and b. That is, for unit path-length

$$A = \varepsilon x = \varepsilon f(K, a, b) \qquad (1)$$

The quadratic solution for $x = f(K, a, b)$ is

$$x = \tfrac{1}{2}\{a + b + K - [(a - b)^2 + K^2 + 2K(a + b)]^{\frac{1}{2}}\} \qquad (2)$$

where the root with the minus sign is taken so that $x \to 0$ as a and $b \to 0$. Differentiation of equation (1) with respect to the parameters required, K and ε, yields

$$\left(\frac{\partial A}{\partial \varepsilon}\right)_K = x \text{ [as in (2)]} \qquad (3)$$

and

$$\left(\frac{\partial A}{\partial K}\right)_\varepsilon = \frac{\varepsilon}{2}\left\{1 - \frac{a + b + K}{[(a - b)^2 + K^2 + 2K(a + b)]^{\frac{1}{2}}}\right\} \qquad (4)$$

We require the K and ε fulfilling conditions:

$$\frac{\partial}{\partial K} \Sigma(A_c - A_m)^2 = 0 \text{ and } \frac{\partial}{\partial \varepsilon} \Sigma(A_c - A_m)^2 = 0 \qquad (5)$$

where A_c is the absorbance calculated from K and ε, and A_m is the experimental value. We put $A_c - A_m = \Delta A$.

We start with initial guesses K_1 and ε_1 (yielding A_{c1}). We write the value of A_c, to be substituted in the equations (5) and hence in equations (7) and (8), in terms of a truncated Taylor series which involves corrections ΔK_1 and $\Delta \varepsilon_1$ to K_1 and ε_1:

$$A_c = A_{c1} + \Delta K_1(\partial A/\partial K)_1 + \Delta \varepsilon_1(\partial A/\partial \varepsilon)_1 \qquad (6)$$

We now calculate ΔK_1 and $\Delta \varepsilon_1$ from the 'normal' equations derived from the conditions in equation (5) above,

$$\sum^n\{A_{c1} + \Delta K_1(\partial A/\partial K)_1 + \Delta \varepsilon_1(\partial A/\partial \varepsilon)_1 - A_m\} \times \\ (\partial A/\partial K)_1 = 0 \qquad (7)$$

$$\sum^n\{A_{c1} + \Delta K_1(\partial A/\partial K)_1 + \Delta \varepsilon_1(\partial A/\partial \varepsilon)_1 - A_m\} \times \\ (\partial A/\partial \varepsilon)_1 = 0 \qquad (8)$$

where differential coefficients with subscript 1 indicate values calculated from K_1 and ε_1. Solution of the simultaneous equations for $\Delta \varepsilon_1$ and ΔK_1 yields $K_2 = K_1 + \Delta K_1$ and $\varepsilon_2 = \varepsilon_1 + \Delta \varepsilon_1$. These values are then used in the second cycle of the iteration which is continued until $\Delta \varepsilon$ and ΔK become arbitrarily small (here $<0.1\%$). The parameters in the final cycle are then the best-fitting values. The only extensions we need note are (i) the cases where several wavelengths are used for absorbance measurements, and thus give rise to several normal equations, and (ii) the expressions for σ_K and σ_ε,

the estimated standard errors of the parameters [3] K and ε, which are derived as:

$$\sigma_K^2 = \frac{\Sigma(\partial A/\partial \varepsilon)^2}{\Sigma(\partial A/\partial K)^2 \Sigma(\partial A/\partial \varepsilon)^2 - \{\Sigma(\partial A/\partial K)(\partial A/\partial \varepsilon)\}^2} \times \\ \frac{\Sigma(\Delta A)^2}{(n - m)} \qquad (9)$$

$$\sigma_\varepsilon^2 = \frac{\Sigma(\partial A/\partial K)^2}{\Sigma(\partial A/\partial K)^2 \Sigma(\partial A/\partial \varepsilon)^2 - \{\Sigma(\partial A/\partial K)(\partial A/\partial \varepsilon)\}^2} \times \\ \frac{\Sigma(\Delta A)^2}{(n - m)} \qquad (10)$$

where $n =$ number of data and $m =$ number of parameters fitted. The root mean square deviation (r.m.s.d.) is given by

$$\text{r.m.s.d.} = \{\Sigma(\Delta A)^2/n\}^{\frac{1}{2}} \qquad (11)$$

One of the vexed and most fundamental questions is that of weighting. While an extensive study can establish accurately what weight should be allotted to each point (including allowance for errors in concentration, which have been neglected in the preceding treatment) it is simplest merely to reject 'bad' points. In this paper those which deviate by more than twice the root mean square deviation are rejected.

The results of our computations from data in the literature, and from our own data, are given in Tables 1 and 2 respectively. In these Tables, n' represents the number of solutions of different composition examined. (Note that n' differs from n if more than one wavelength is used. In our view n' is more important than n since, though observation at an extra wavelength increases n, it also increases m, the number of parameters, and the benefit is reduced.) The fourth column gives rounded values of the lowest concentration taken; the factor in brackets shows by how much this was increased [e.g. (×10) indicates that the highest concentration taken was ten times the lowest]. The values of ε are given in brackets immediately below the K_{ass} values to which they correspond. By 'original' is meant the value obtained by the original author(s) in the given reference, and 'least-squares' indicates the value to be from our own computations. The values in the latter column are each followed by $\pm\sigma_{K_{ass}}$ (or $\pm\sigma_\varepsilon$), which are the statistical errors in the parameters attributed to random errors in the observations. (Any inadequacies in the basic functions e.g. non-obedience to Beer's law, or neglect of interactions which might be interpreted by an additional associative equilibrium, would contribute to the computed σ values: use of the least-squares method implies the assumed absence of such deviations. Notes 1 and 3 for Table 1 are relevant here.)

DISCUSSION

While several hundred K_{ass} values for weak complexes appear in the literature, Table 1 includes nearly all those for which the actual absorbance data are reported. In Table 1, there are often appreciable discrepancies between the authors' estimate and our least-

TABLE 1

Ref.	n'	Reactants	Concn. (mole l.$^{-1}$) ($\times$ variation)	K_{ass} (l. mole^{-1}) [Values of ε (l. mole^{-1} cm.$^{-1}$) in parentheses]		R.m.s.d.	Notes
				Original	Least-squares		
9	10	Naphthalene	0·01 ($\times$5)	2·29	6·94 $\pm$ 1·36	0·024	(2)
		Picric acid	0·01 ($\times$5)	(377)	(153 $\pm$ 20)		
10	9	Indole	0·11 ($\times$3)	2·86	2·82 $\pm$ 0·08	0·0025	(1)
		Chloranil	2·4 $\times$ 10^{-3} ($\times$1)	(1510)	(1526 $\pm$ 30)		
11	6	Toluene	0·37 ($\times$3)	0·92	0·918 $\pm$ 0·029	0·0037	(1)
		2,3-Dichloro-5,6-dicyano-p-benzoquinone	0·78 $\times$ 10^{-3} ($\times$1)	(2332)	(2236 $\pm$ 40)		
12	9	Tetramethyl-p-phenylenediamine	0·11 ($\times$3)	4·1	4·04 $\pm$ 0·10	0·0018	(1)
		Tricyanobenzene	2·4 $\times$ 10^{-3} ($\times$1)	(350)	(355 $\pm$ 5)		
1	7	Benzene	0·5 ($\times$21)	0·163	0·159 $\pm$ 0·003	0·0066	
		Iodine	3·3 $\times$ 10^{-5} ($\times$13)	(15,060)	(15,307 $\pm$ 197)		
13	3	NN-Dimethylacetamide	0·05 ($\times$4)	2·6	2·79 $\pm$ 0·14	0·0006	
		Iodine	9·2 $\times$ 10^{-3} ($\times$1)	(—)	(74 $\pm$ 3)		
14	9	Diphenylamine	0·08 ($\times$5)	0·51	0·500 $\pm$ 0·008	0·0004	
		Trinitrobenzene	0·0019 ($\times$1)	(1391)	1391 $\pm$ 20		
	8	Diphenylamine	0·0024 ($\times$1)	0·49	0·505 $\pm$ 0·016	0·0006	(3)
		Trinitrobenzene	0·08 ($\times$4)	(1653)	1653 $\pm$ 47		
	17	Diphenylamine	0·0024 ($\times$200)		1·32 $\pm$ 0·56	0·025	
		Trinitrobenzene	0·0019 ($\times$150)		685 $\pm$ 155		
15	4	Pyrene	0·03 ($\times$2·5)	36·5	42·3 $\pm$ 7·7	0·0018	(1)
		Iodine	3·2 $\times$ 10^{-4} ($\times$1)	(161)	(141 $\pm$ 9)		
15	4	Anthracene	0·14 ($\times$1·5)	52·4	8·3 $\pm$ 4·6	0·0028	
		Iodine	1·9 $\times$ 10^{-4} ($\times$1)	(112)	(261 $\pm$ 115)		
15	4	Biphenyl	0·04 ($\times$4)	0·37	0·14 $\pm$ 0·13	0·00088	(1)
		Iodine	8 $\times$ 10^{-4} ($\times$1)	(4000)	(10,200 $\pm$ 9100)		
15	4	Phenanthrene	0·013 ($\times$2)	1·06	2·1 $\pm$ 4·6	0·0015	(1)
		Iodine	6·5 $\times$ 10^{-4} ($\times$1)	(1492)	(770 $\pm$ 1160)		
16	5	Nicotinonitrile	0·033 ($\times$10)	1·73	1·83 $\pm$ 0·19	0·0068	(1)
		Iodine	1·4 $\times$ 10^{-3} ($\times$1)	(1340)	(1223 $\pm$ 91)		
17	8	Thiocyclobutane	8·2 $\times$ 10^{-4} ($\times$3)	87	97·4 $\pm$ 12·7	0·0041	
		Iodine	4·8 $\times$ 10^{-4} ($\times$4)	(several)	(several)		
18	4	Dimethylselenide	4·5 $\times$ 10^{-4} ($\times$40)	471	442 $\pm$ 25	0·0052	
		Iodine	4·5 $\times$ 10^{-4} ($\times$20)	(several)	(several)		
18	4	Dimethylselenide	3·6 $\times$ 10^{-4} ($\times$12)	2·5 $\times$ 10^6	∞?	0·0037	
		Bromine	3·5 $\times$ 10^{-4} ($\times$20)	(several)	(several)		
8	10	Hexamethylbenzene	0·014 ($\times$10)	0·64	0·648 $\pm$ 0·092	0·0045	(1)
		Carbon tetrachloride	0·08 ($\times$1)	(872)	(902 $\pm$ 114)		
7	5	Mesitylene	0·0058 ($\times$1)	0·112	0·144 $\pm$ 0·017	0·0033	(1)
		Carbon tetrachloride	0·16 ($\times$8)	(8100)	(7125 $\pm$ 713)		
6	5	Benzene	0·089 ($\times$1)	0·009	0·001 $\pm$ 0·02	0·001	(1, 4)
		Carbon tetrachloride	0·16 ($\times$8)	(859)			

Notes on the tabulation of fitted parameters. (1) Where only one concentration of one of the reactants has been used, the extent of association (whether 1 : 1, 2 : 1, or other, complex) must be in doubt.

(2) Conrow's criterion (see Discussion section) would require the rejection of these eminently satisfactory K_{ass} and ε values.

(3) The first two entries for this system involve two separate measurements, first with one reactant concentration constant, then with the other. The K_{ass} values agree well and the root mean square deviation (r.m.s.d.) values are low, but different ε values are obtained. The third entry involves the pooling of the preceding data and the assumption of a constant ε; judged from any criterion the fit deteriorates, and there is *prima facie* evidence here for disobedience to Beer's law (extinction coefficient differing for different ranges).

(4) For this system high precision in absorbance ($\pm 0·1\%$) was claimed, but the equally important precision, of solution concentrations, is not stated. No fit was in fact obtained, *i.e.* insufficient data are available to achieve $\Delta\varepsilon/\varepsilon$ and $\Delta K/K <$ 0·1%. The $K_{ass} \pm \sigma_{K_{ass}}$ value quoted reproduces the experimental absorbances with an r.m.s.d. of 0·001; if the absorbance error was any larger a yet wider range of K_{ass} would be indicated. Person's view [19] that these data give a K_{ass} indistinguishable from zero might better be replaced by the conclusion that $K_{ass} < 0·02$ l. mole^{-1}.

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squares value, and such discrepancies would doubtless also occur with some of the undocumented literature assessments. Often values, derived rather subjectively, are reported without the original measurements upon which they are based. This unscientific procedure could be counteracted by insistence on the part of referees that all these relevant, indeed essential, details should be included, or deposited at libraries.

Though approximate graphical methods appear adequate when $\sigma_K < 20\%$, they do not furnish values of σ_K for assessment. Some of the literature data could be

deepest) minimum of r.m.s.d. This danger can be obviated by repeating the calculation with wide variations of the starting values K_1 and ε_1.

APPENDIX

While our method is similar to Wentworth's,[4] we do not concur with his support of Conrow's conclusions [5] concerning the errors resulting from the rounding-off of data, nor do we concur with Conrow's views [5] on the rejection of data (cf. Note 2 on Table 1).

Conrow fitted K and ε by essentially a trial and error

TABLE 2

n'	Reactants	Concn. (mole l.⁻¹) (× variation)	$K_{ass} \pm \sigma_{K_{ass}}$ (l. mole⁻¹)	$\varepsilon \pm \sigma_\varepsilon$ (l. mole⁻¹ cm.⁻¹)	R.m.s.d.	λ (nm)	Notes
11	Carbon tetrachloride Benzene	0·06 (×3) 0·05 (×14)	0·076 ± 0·057	4070 ± 2840	0·010	220	(1)
93	Carbon tetrachloride p-Xylene	0·06 (×17) 0·04 (×20)	0·136 ± 0·018	several	0·0098	232—238	(2)
97	Carbon tetrachloride m-Xylene	0·02 (×50) 0·024 (×33)	0·112 ± 0·028	several	0·0074	232—238	(2)
22	Carbon tetrachloride Mesitylene	0·08 (×2·5) 0·05 (×10)	0·252 ± 0·036	several	0·0057	234—238	(3)
10	Carbon tetrachloride Hexamethylbenzene	0·1 (×5) 0·026 (×9)	0·550 ± 0·160	several	0·0169	242—246	(4)

Notes. (1) At wavelengths more distant from the maximum, K_{ass} values of 0·047 ± 0·056 and 0·033 ± 0·062 were obtained. Though clearly poorly determined, they support the value tabulated (the lower end of the given range favoured).

(2) Extinction coefficients in l. mole⁻¹ cm.⁻¹ for the p-xylene complex are (to within ca 3%) 3144 (232 nm.), 2440 (234 nm.), 1871 (236 nm.), and 1456 (238 nm.). For the m-xylene complex (same wavelengths) the values are 3850, 2989, 2283, and 1698 respectively.

(3) Extinction coefficients are 2723 (234 nm.), 2268 (236 nm.), 1820 (238 nm.), within ca. 4%.

(4) A low carbon tetrachloride concentration was used in this determination in view of evidence [8] for small amounts of a 2 : 1 complex. Extinction coefficients are 1150 (242 nm.), 1109 (244 nm.), 1062 (246 nm.), within ca. 10%.

(1), (3), and (4). Though the values here differ somewhat from the K_{ass} values given for these systems in Table 1, the discrepancies are not seriously beyond the $\sigma_{K_{ass}}$ limits. Our results are derived from a larger number of measurements and employed wider changes in the variables. Values of K_{ass} are plotted in Figure 1 against n_{Me}, the number of methyl groups on the benzene ring.

improved by extension of the ranges of concentrations, since these ranges have often been unnecessarily curtailed in order to validate the approximations made in the original computations.

The number of solutions used, n', is very important in the determination of the reliability of the parameters, and ranks in importance with the range of variation of concentrations. While a detailed examination of the particular properties of each system under study should be made in order to assess the requirements of maximum precision, for currently typical systems and contemporary spectrophotometers we can summarily conclude that $n' = 4$ or 5 is much too low, $n' = 10$—15 will often suffice, and that $n' = ca.$ 25 is probably most satisfactory. If the parameters are not well determined by ca. 25 measurements, the remedy lies not in further repetition but in extending the range, or improving the precision or type of measurement, or finding a more correct function.

The major fitting error arises when the solutions of the normal equations correspond to a false (i.e. not the

procedure; one parameter, say K, was chosen and its concomitant, say ε, was then the corresponding least-squares fit. Thus for each choice of K, absorbances $A(\text{calc})$ could be calculated for comparison with $A(\text{obs})$, with the best choice of K and concomitant ε giving the lowest value of $\Sigma\{A(\text{calc}) - A(\text{obs})\}^2$ in all the trials. This procedure should, and does, yield K and ε values equal to those obtained by our method, but does not yield the errors in these parameters. Instead Conrow defines a ' sharpness ' parameter S which is the % increase in $\Sigma\{A(\text{calc}) - A(\text{obs})\}^2$ which would result from an (arbitrary) 10% change in K from its best-fit value; $S < 20$ was taken as an arbitrary criterion for rejecting data. The objection to such a criterion is perhaps best stated by the assertion that the sharpness S for a particular set of measurements will in general not be improved by an increase in the number n of measurements made (above some small minimum number), whereas the statistical errors σ_K and σ_ε, in which n appears in the denominators of their defining expressions, must decrease with n [albeit slowly at high n (see theory)].

As a check on their computer program, Conrow et al. took an arbitrary set of concentrations of a donor and acceptor, assigned both an arbitrary extinction coefficient to,

and an association constant for, their 1 : 1 complex, and calculated 'synthetic' absorbances which would be observed for such a system. The computer was then programmed to retrieve, from the synthetic absorbances and the concentrations, the values of K and ε originally assumed.

For one set of measurements the rounding-off of absorbances to the number of digits experimentally accessible apparently introduced a discrepancy of 8% between the fitted and the original K values. This is an enormous and alarming error for absorbances measurable to three figures. Recalculation of Conrow's synthetic absorbances shows the set in question to range from 0·047 to 7·99, half of which are >2 (and thus scarcely typical). The combination of rounding-off the higher values to the second decimal place (which place is vital for the lower absorbances), and the appreciable contribution to total absorbance of uncomplexed reactant, effectively introduces errors of several per cent into much of the data. The 8% fitting error is an artefact avoidable by ensuring an adequate change in absorbance due to complex formation, and by the (in fact experimentally inescapable) limitation of absorbances to a narrower range. To fit data of widely varying order of magnitude square fractional deviations, not square deviations, must be minimised.

Finally, Conrow inferred that errors of 1% in solution concentrations might cause errors of 50% in the fitted K_{ass}. We need only point out here that a mere three solutions were taken [5] to generate this data, and that if the inexact concentrations of A and B are varied by less than two-fold, as here, K_{ass} will, not surprisingly, be retrieved only as an order-of-magnitude estimate.

EXPERIMENTAL

Solutions of benzene and carbon tetrachloride (of spectroscopic quality) were made up by weight in cyclohexane; sulphur was removed from the methyl-substituted benzenes with H_2SO_4, KOH, and distillation from mercury; hexamethylbenzene (Aldrich) was successively recrystallised from ethanol. Concentration errors from evaporation were assessed as $<1\%$. Absorbances [20] were measured at 25°C on a Unicam SP 500 at or near the maxima of the new charge transfer bands, in UV-01 cells (Research and Industrial Instruments Company), length 0·01—0·1 cm. Cell lengths were measured by micrometer. The blank cell contained solutions of either donor or acceptor, to enhance the absorbance increments due to complex formation. Measurements were at or near maxima, which were observed at *ca.* 216 nm. (benzene), 230 (xylenes), 235 (mesitylene), and 242 nm. (hexamethylbenzene). (Values are
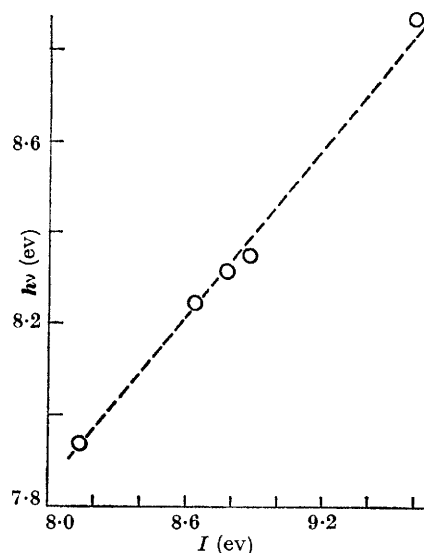

FIGURE 2   Observed charge-transfer maxima $h\nu$ *vs.* ionisation potential I of donor molecules (ref. 21)

approximate because of overlapping absorptions by donors, acceptors, and complex; their correlation with the ionisation potential of the donor [21] (Figure 2) supports the characterisation of the complexes as the charge-transfer type.)

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