A FIRST ITERATE FOR ASSOCIATION CONSTANTS

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ABSTRACT.—A new initialization procedure for iterative spectroscopic determinations of association constants is derived. It is proven that this initialization is valid when the concentration of dimer greatly exceeds the concentration of monomer. Numerical results are presented to substantiate the derivation. The effects of numerical manipulations are discussed.

Keefer and Andrews (1952) have derived a spectrophotometric iteration method for the determination of concentration constants of charge transfer complexes. Musulin, et al., (1962) have discussed the convergence failure of the method after it had been specialized (de Maine, et al. (1957), (1960a)) to determine concentration constants of association reactions. The purpose of this paper is to consider what effect there is upon the choice of the first iterates if the system deviates but slightly from Beer's law (Prutton and Maron (1951), pp. 756, 758). Although convergence failure destroys the ultimate utility of the method, there are other methods, e.g., Non-linear Least Square Method (Scarborough, (1950) pp. 463-9), which demand a good initial guess of the unknowns. The present analysis leads, fortuitously, to an initial iterate of the concentration constant which may be useful under the assumptions of this derivation. Finally, numerical calculations are presented in order to verify the theory.

The system to be investigated is the simple dimerization

$$2A \rightleftarrows A_2 \qquad (1)$$

In order to specify the notation, the equations of the iteration scheme, as taken from Musulin, et al., (1962) are given in Equations (2) to (5).

$$\frac{C^2_a}{D_C} = \frac{2}{\epsilon_C}(2C_a - C) + \frac{1}{K\epsilon_C} \qquad (2)$$

$$C = \frac{4KC_a + 1 - \sqrt{8KC_a + 1}}{4K} \qquad (3)$$

$$\frac{D}{C_a - C} = K\epsilon_C (C_a - C) + \epsilon_M \qquad (4)$$

$$D_C = \tfrac{1}{2} C\epsilon_C \qquad (5)$$

where C_a is the total solute concentration in monomeric units, $\frac{1}{2}$ C is the equilibrium dimer concentration, K is the concentration constant for Equation (1), (insufficient information is available concerning activity coefficients to be able to write a thermodynamic equilibrium constant), D and D_C are the absorbances (optical densities) of the solution and the dimer, respectively, and ϵ_C and ϵ_M are

the molar absorptivities (extinction cofficients) of the dimer and monomer, respectively. In these equations as well as the succeeding material, it is assumed that measurements are made in cells of unit path length. Should this not be so, the actual molar absorptivity would have to be obtained from the calculated molar absorptivity thru division by the path length.

Beer's Law and Initialization

In the derivation of Equations (2) to (5), the assumption has been made that the total absorbance is the sum of the absorbances of the monomer and dimer (Musulin, et al. (1962)). This assumption is stated mathematically as

$$D = D_M + D_C \tag{6}$$

where D_M is the monomeric absorbance given by

$$D_M = (C_a - C)\,\epsilon_M \tag{7}$$

Then

$$D = (C_a - C)\,\epsilon_M + \tfrac{1}{2}\,\epsilon_C\,C \tag{8}$$

If no equilibrium existed, Equation (8) would reduce to a simple statement of Beer's law. Also, Foley, et al., (1964) have shown that low members of the homologous nitroparaffin series obey Beer's law even though they are thought to undergo the reaction described in Equation (1). In such a case, if two species did occur, the fortuitous adherence to Beer's law would be described by

$$D = \bar{\epsilon} C_a \tag{9}$$

where $\bar{\epsilon}$ is an average molar absorptivity. It is of particular interest to see what effect the actual or accidental adherence to Beer's law would have on the initial values of the iterates.

Equation (9) may be obtained from Equation (8) by assuming

$$C = \delta C_a \tag{10}$$

where δ is a temperature dependent proportionality constant. Direct substitution of Equation (10) into Equation (8) gives

$$D = [\epsilon_M + \delta\,(\tfrac{1}{2}\,\epsilon_C - \epsilon_M)]\,C_a \tag{11}$$

which shows that

$$\epsilon = \epsilon_M + \delta\,(\tfrac{1}{2}\,\epsilon_C - \epsilon_M) \tag{12}$$

It may be pointed out that the concentration constant, which is

$$K = \frac{\tfrac{1}{2}\,C}{(C_a - C)^2} \tag{13}$$

becomes

$$K = \frac{\delta}{2C_a\,(1-\delta)^2} \tag{14}$$

under the assumption of Equation (10). Further, the special cases of the system containing all dimer or all monomer follow immediately from Equation (10).

If the system contains no dimer, $C = 0$; and this is equivalent to assuming $\delta = 0$. Then

$$\begin{aligned} &\lim_{\delta \to 0} D = \epsilon_M C_a \\ &\lim_{\delta \to 0} K = 0 \end{aligned} \tag{15}$$

Equations (15) are precisely the description of a system containing all monomer.

If

$$\delta = 1 - \eta \tag{16}$$

where η is a constant, then the system containing all dimer is described by the assumption that $\eta = 0$. For then

$$\begin{aligned} &\lim_{\eta \to 0} D = \tfrac{1}{2}\,\epsilon_C\,C_a \\ &\lim_{\eta \to 0} K = \infty \end{aligned} \tag{17}$$

which is the description of a system containing all dimer.

Returning to the general problem, it is of interest to form the ratio, D/D_C.

$$\frac{D}{D_C} = \frac{[\epsilon_M + \delta\,(\tfrac{1}{2}\,\epsilon_C - \epsilon_M)]\,C_a}{\tfrac{1}{2}\,\epsilon_C\,C_a\,\delta} \tag{18}$$

or

$$\frac{D}{D_C} = 1 + \frac{2\epsilon_M}{\epsilon_C}\left(\frac{1}{\delta} - 1\right) \tag{19}$$

The starting point of the iteration scheme (Musulin, et. al. (1962)) is usuly made by assuming in Equation (2) that

$$D_C \cong D \tag{20a}$$

$$C \cong 0 \tag{20b}$$

However, from Equations (10) and (19), it is possible to substitute directly for

C and $1/D_C$ in Equation (2). After rearranging terms, one obtains

$$\frac{C_a^2}{D} = \frac{(2-\delta)\,C_a}{(\tfrac{1}{2})\,\epsilon_C + \epsilon_M\left(\frac{1}{\delta}-1\right)} + \frac{1}{K\left[\epsilon_C + 2\epsilon_M\left(\frac{1}{\delta}-1\right)\right]} \qquad (21)$$

Then, using Equation (12). Equation (21) becomes

$$\frac{C_a^2}{D} = \frac{(2-\delta)\,C_a}{\frac{1}{\delta}\bar{\epsilon}} + \frac{1}{\frac{2}{\delta}\bar{\epsilon}K} \qquad (22)$$

or

$$\frac{C_a^2}{D} = \frac{(2-\delta)\,\delta\,C_a}{\bar{\epsilon}} + \frac{\delta}{2\bar{\epsilon}K} \qquad (23)$$

Equation (23) represents a straight line if one plots C_a^2/D *vs.* C_a. The slope, m, and the intercept, b, of the straight line are given by

$$m = \frac{(2-\delta)\,\delta}{\bar{\epsilon}} \qquad (24)$$

$$b = \frac{\delta}{2\bar{\epsilon}K} \qquad (25)$$

Equation (24) is a quadratic equation in δ with the solution

$$\delta = 1 \pm \sqrt{1 - m\bar{\epsilon}} \qquad (26)$$

Only the negative sign has physical significance since C cannot be greater than C_a.

Therefore, it is possible, if the system nearly obeys Beer's law, to obtain an estimate, $K^{(1)}$, for K. This information alone is insufficient to continue the iteration procedure since to return to Equation (2) one needs D_C. Yet, Equations (5), (6), and (7) form a system of three equations in four unknowns giving a singly infinite set of values for D_C. Clearly, some further information would be necessary to select the proper value of D_C.

Limitation of the Use of Beer's Law

Equation (9) may be obtained from Equation (8) in other ways than by using Equation (10). The various means are given by choosing (i) $C = 0$, (ii) $C_a - C = 0$, and (iii) $\epsilon_C = 2\epsilon_M$. The assumption of Equation (10) is equivalent to being in the region of $C_a - C = 0$. This may be seen mathematically by insertion of Equation (9) in Equation (23). After substitution,

$$\frac{C_a}{\bar{\epsilon}} = \frac{(2-\delta)\,\delta}{\bar{\epsilon}} C_a + \frac{\delta}{2\epsilon K} \qquad (27)$$

Equation (27) is an identity which is satisfied only by the conditions, $\delta = 1$ and $K = \infty$. Consequently, $K^{(1)}$ found from the use of Equation (23) is only useful if $K >> 1$. For the case under discussion and for the starting point given by Equation (20), $K^{(1)}$ is found from plots of C_a^2/D *vs.* C_a. Without a true convergence scheme, one cannot be sure whether a $K^{(1)}$ from Equation (23) really describes the system or whether $K^{(1)}$ is determined simply by Equation (27).

The same conclusions are obtained without limiting the functional form as in Equation (8). For example, if the solution is nearly all dimer, one can let the monomer concentration be

$$C_a - C = \eta \qquad (28)$$

where η is a small quantity which vanishes in the limit. Now as before, the quotient D/D_C is formed.

$$\frac{D}{D_C} = 1 + \frac{2\eta\epsilon_M}{\epsilon_C\,(C_a - \eta)} \qquad (29)$$

Again, $1/D_C$ from Equation (29) and $(2\,C_a - C)$ derived from Equation (28) are substituted into Equation (2) yielding

$$\frac{C_a^2}{D}\left[1 + \frac{2\eta\epsilon_M}{\epsilon_C\,(C_a - \eta)}\right] = \frac{2}{\epsilon_C}(C_a + \eta) + \frac{1}{\epsilon_C K} \qquad (30)$$

If $\eta \rightarrow 0$ in Equation (30), one obtains a straight line plot of C^2_a/D *vs.* C_a with slope, m, and intercept, b, given by

$$m = \frac{2}{\epsilon_C} \qquad b = \frac{1}{K\epsilon_C} \tag{31}$$

It should be noted that the starting assumptions, Equations (20), which had been used, heretofore, are contradictory in that Equation (20a) implies all dimer and Equation (20b) implies all monomer. By putting these conditions into Equation (2), the first iterates can be compared to those obtained by the condition given in Equation (28). (The subscript refers to the equation giving rise to the iterate).

$$\epsilon^{(1)}_{28} = \tfrac{1}{2}\,\epsilon^{(1)}_{20} \qquad K^{(1)}_{28} = K^{(1)}_{20} \tag{32}$$

Consequently, one would obtain the same $K^{(1)}$ but again, with either starting assumption, reasoning similar to that used to obtain Equation (27) shows that $K>>1$.

Numerical Results

Several calculations were performed in order to ascertain if the conclusions reached analytically would be verified with typical data. The majority of the data were those from the nitroparaffin study of Foley, et al. (1964). However, several other experiments were used in order to broaden the base upon which the conclusions are based. The details of the various experimental procedures may be found in the original papers. The calculations were performed upon an IBM 1620 computer. All programs were written in FORTRAN II.

Equation (23) is derived under the assumption that two solute species coexisted in such a manner that the absorbance of the solution obeyed Beer's Law. Consequently, one would expect that plots of C^2_a/D *vs.* C_a become more linear as plots of D *vs.* C_a become more linear. Since Foley, et al., (1964) have shown that Pearson's Correlation Coefficient is a good means of determining linearity from chemical data, the same technique was used to test these plots. The correlation coefficients, r_1 and r_2, were calculated at each wave length for plots of D *vs.* C_a and $C^2_a/4D$ *vs.* $2C_a$, respectively. Although the latter involves a change of scaling (thought to be necessary in originating the investigation), the scaling does not alter the computation of r_1 and r_2. These values were averaged over all wave lengths involving the same concentration values to give the average correlation coefficients, $\bar{r}_1$ and $\bar{r}_2$. The average correlation values are tabulated in Table 1 along with quantities defining the specific experiments.

Table 1 clearly indicates that Equation (23) is linear if the system obeys Beer's Law. As long as the system nearly obeys Beer's Law, there is a direct proportionality between the two correlation averages. However, if the data deviates widely from Beer's Law (and this means only a value of $r < .995$) (Foley, et. al. (1964)), then Equation (23) shows essentially no linearity, e.g., consider the first two entries of $C_2H_5NO_2$. It should be noted that certain data which are known to be experimentally poor have been included in order to extend the range of the calculations. This has been done using the hypothesis that a

TABLE 1.—Averaged Pearson Correlation Coefficients of Various Binary Solutions for Different Concentration Ranges.

Solute	Solvent	Concentration Range (10^2 M)	$\bar{r}_1$	$\bar{r}_2$
CH_3NO_2	CCl_4	0.6 - 3.0	.99471	.99501
		1.0 - 3.0	.99836	.99851
		1.5 - 3.0	.99982	.99981
		10. - 25.	.99939	.99946
		1.0 - 5.0	.99902	.99896
		6.58 - 1864	.97866[a]	.98377[a]
	H_2O	1.0 - 5.0	.99538	.99447
$C_2H_5NO_2$	CCl_4	0.8 - 3.0	.94468	.60541
		1.0 - 5.0	.97460	.76778
		1.0 - 3.0	.99948	.99947
		1.0 - 5.0	.99673	.99481
	H_2O	1.0 - 5.0	.99820	.99714
1-$C_3H_7NO_2$	CCl_4	1.25 - 3.0	.96614	.98626
		12.5 - 30.	.99761	.99666
2-$C_3H_7NO_2$[b]	CCl_4	1.25 - 3.0	.99755	.99813
		12.5 - 30.	.99883	.99919
2,5-dimethylpyrazine[c]	25% H_2SO_4	.002 - .01	.99998	.99998
2-methylpyrazine[c]	H_2O	.002 - .01	.99613	.99507
Pyrazine[c]	75% H_2SO_4	.002 - .01	.99995	.99995
Cyclohexanol[d]	CCl_4	0.10 - 5.65	.98854	.99338
CH_3NO_2[e]	CCl_4	38 - 1851 (3.29 μ)	.98952	.97332
CH_3NO_2[e]	CCl_4	38 - 1851 (3.42 μ)	.99823	.99734

[a]Pestemer and Fruhwirth (1937). [b]From rounded data. [c]Chia (1960).
[d]Masschelein (1962). [e]de Maine (1960b).

computer would not differentiate between deviations originating from chemical interaction and those from an inexperienced experimenter.

The foregoing supports previous experimental work that plots of C^2_a/D *vs.* 2 C_a were linear in the range where Beer's Law was obeyed to within two per cent (de Maine, et. al. (1960a)).

Under the assumption that the solution obeys Beer's Law (or nearly so), it has been proposed (follow Equation (27)) that $K >> 1$. However, if this is so, serious computational difficulties must occur. If $K >> 1$, then the intercept, b, of Equation (27) must approach zero. This in fact does occur in this investigation for $b \sim 0(10^{-5})$. Unfortunately, if b is this order of magnitude, a slight experimental error could cause a value of $b < 0$. Again, it may also be stated that as $b \rightarrow 0$, one would expect random fluctuations about the limiting value which would also give rise to values of $b < 0$.

A negative value of b results in a physically unreal value of $K^{(1)}$. Nevertheless, in the present work the average value of the first iterate, $K^{(1)}$, including any negative values which may occur, is calculated. Now two questions must be answered. Firstly, is the value of $\overline{K}^{(1)}$ reasonable? Reasonability could be ascertained by a possible correlation of $\overline{K}^{(1)}$ values of different homologues and/or the correlation of $\overline{K}^{(1)}$ values

in different solvents. Secondly, regardless of the value of $\overline{K}^{(1)}$, is it true that $\overline{K}^{(1)}$ is independent of wave length? The answer to the latter question is aided by the calculation of the per cent deviation (% Deviation = $(\overline{K}^{(1)} - \overline{\overline{K}}^{(1)}/\overline{K}^{(1)}) \times 100$). The pertinent quantities are given in Table 2.

It is clear from Table 2 that no pattern emerges from the $\overline{K}^{(1)}$ values except chaos. Some physically unreal values occur; some large values occur; and some small values, resulting from the fortuitous cancellation of positive and negative values, occur.

In no case does $\overline{K}^{(1)}$ show a functional dependence upon wave length. On the other hand, there is usually great randomness, as indicated by the large values of the average deviations. A close comparison of the values of per cent deviation and the values of $\bar{r}_1$ leads to the conclusion that as Beer's Law becomes more completely satisfied by the absorbances of the solution, the calculated values of $K^{(1)}$ become more random. In fact, only the very poor data of $C_2H_5NO_2$ ($\bar{r}_1 = .94468$), (later shown to be erroneous by remeasurement), and the questionable 1-$C_3H_7NO_2$ data ($\bar{r} = .96614$) showed any lack of randomness in the $\overline{K}^{(1)}$ values. It appears that once Beer's Law is obeyed, or nearly so ($\bar{r}_1 \geqq .995$), the amount of deviation is completely random.

The cancellation of positive and negative values of $K^{(1)}$ in obtaining $\overline{K}^{(1)}$ may be avoided by calculating the average, $|\overline{K}^{(1)}|$, of the absolute values of $K^{(1)}$. Then one would expect either that $|\overline{K}^{(1)}| >> 1$ or that $K >> 1$. The former resulted upon division by a value of $b << 1$. The latter was proven, by analysis, to result from Equation (27). This becomes more true as the plot of C^2_a/D *vs.* C_a approaches linearity (as measured by $\bar{r}_2$). The values of $|\overline{K}^{(1)}|$ are given in Table 3.

TABLE 2.—The Averaged First Iterate of each Concentration Constant for Various Binary Solutions.

Solute	Solvent	Concentration Range (10^2 M)	$\overline{K}^{(1)}$ *l*/mole	Deviation (%)	$\bar{r}_1$
CH_3NO_2	CCl_4	0.6 - 3.0	781	58	.99471
		1.0 - 3.0	—254	48	.99842
		1.5 - 3.0	267	30	.99982
		10. - 25.	—176	52	.99939
		1.0 - 5.0	764	61	.99902
	H_2O	1.0 - 5.0	338	187	.99538
$C_2H_5NO_2$	CCl_4	0.8 - 3.0	11	2	.94468
		1.0 - 5.0	11	..[b]	.97460
		1.0 - 3.0	2460	120	.99948
		1.0 - 5.0	149	97	.99673
	H_2O	1.0 - 5.0	716	113	.99820
1-$C_3H_7NO_2$	CCl_4	1.2 - 3.0	—93	15	.96614
		12. - 30.	—42	46	.99761
2-C_3H_7NO[a]$_2$	CCl_4	1.2 - 3.0	—377	54	.99755
		12. - 30.	—38	34	.99883

[a]Rounded data.
[b]Single reading, thus no deviation.

An inspection of the values in Table 3 shows that, in general, $K^{(1)} >> 1$ for values of $\bar{r}_2 > 0.995$. The decision as to largeness is based upon the fact that values of $K \sim 100$ correspond to approximately 90% dimer. Further, a comparison of the values of $|\overline{K}^{(1)}|$ and $\bar{r}_2$ leads to the same conclusions that are deduced from Table 2.

Numerical Experimentation

In any practical analysis where numerical work enters the border regions of limiting validity, it behooves one to carry forth numerical experimentation to eliminate any possible numerical influences upon the conclusions. Several such experiments have been carried out in connection with the present investigation.

For several of the solutions, error limits were assigned to the measured concentration values (Foley, et. al. (1964)). All quantities were calculated with concentrations given to four significant figures, concentrations with the assigned error added (to four significant figures), concentrations with the assigned error subtracted (to four significant figures), and finally the concentrations rounded to the values assigned in Tables 1 to 3 to the column designated Concentration Range. The median values (uncorrected four figure values) were used, except as noted, to calculate the quantities in Tables 1 to 3.

Table 4 tabulates the effect of the various numerical changes upon the pertinent quantities for some sample nitromethane and nitroethane solutions. These selections represent the typical behavior which was found.

The most startling fact shown in Table 4 is that, if the solution obeys Beer's Law (or nearly so), the calculation of $K^{(1)}$ is extremely sensitive to the error in the dependent variable and even more so, if possible, to the number of significant figures retained. Since the errors involved are of the order of 1 to 2%, a twenty-five per cent change in $K^{(1)}$ is unreasonable. Foley, et

Table 3.—The Averaged Absolute Value of the First Iterate of each Concentration Constant for Various Binary Solutions.

Solute	Solvent	Concentration Range (10^2 M)	$\lvert\overline{K}^{(1)}\rvert$ *l*/mole	$\bar{r}_2$
CH_3NO^2	CCl_4	0.6 - 3.0	945	.99501
		1.0 - 3.0	327	.99859
		1.5 - 3.0	320	.99981
		10. - 25.	176	.99946
		1.0 - 5.0	801	.99896
	H_2O	1.0 - 5.0	676	.99447
$C_2H_5NO_2$	CCl_4	0.8 - 3.0	11	.60541
		1.0 - 5.0	11	.76778
		1.0 - 3.0	2456	.99947
		1.0 - 5.0	181	.99481
	H_2O	1.0 - 5.0	986	.99714
1-$C_3H_7NO_2$	CCl_4	1.2 - 3.0	93	.98626
		12. - 30.	48	.99666
2-$C_3H_7NO_2$[a]	CCl_4	1.2 - 3.0	397	.99813
		12. - 30.	38	.99919

[a]Rounded data.

TABLE 4.—The Effect of Experimental Error Upon Pertinent Calculated Quantities for Selected Binary Solutions.

Solute	Solvent	Concentration Manipulation	$\lvert\overline{K^{(1)}}\rvert$ *l*/mole	$\overline{K^{(1)}}$ *l*/mole	Deviation (%)	$\bar{r}_1$	$\bar{r}_2$
CH_3NO_2	CCl_4	Rounded	1523	1399	63	.99388	.99454
		Error Added	773	586	63	.99472	.99499
		Median	945	782	58	.99471	.99501
		Error Subtracted	922	741	63	.99487	.99517
CH_3NO_2	CCl_4	Rounded	2180	1340	183	.99990	.99990
		Error Added	199	120	107	.99944	.99941
		Median	320	267	31	.99982	.99981
		Error Subtracted	419	384	56	.99987	.99987
$C_2H_5NO_2$	CCl_4	Rounded	11	11	2	.94699	.60437
		Error Added	11	11	2	.94504	.60502
		Median	11	11	2	.94468	.60541
		Error Subtracted	12	12	2	.94357	.60131

al., (1964) point out that the same sensitiveness does not occur in the calculation of the molar absorptivities. The present numerical experimentation has focused upon the $K^{(1)}$ values since the analysis has proven that they, not $\epsilon^{(1)}$ would be the most sensitive. On the other hand, if deviations from Beer's Law occur, Table 4 clearly shows the insensitiveness of $K^{(1)}$.

If $K^{(1)} >> 1$ (here the largeness is a true numerical largeness, $\sim 0(10^3)$, not a physically significant largeness, $\sim 0(10^2)$), the per cent deviation remains essentially constant even if the system obeys Beer's Law. However, if $K^{(1)} > 1$, then the denominator in the calculation of per cent deviation does not provide sufficient stability to keep that quantity constant.

Finally the correlation coefficients remain essentially constant under all changes in the dependent variable. This reflects the usefulness of the correlation coefficient (if one is careful in its use) in chemical and physical problems (Gottschalk, (1962)). Alternatively, one could say that the degree of "fit" to Beer's Law is invariant within experimental error.

In the original investigation, several chemical experiments were attempted in order to fix variables. In light of the preceding conclusions these, too, must be reduced to numerical experimentation. That is, no chemical information was found but more is learned concerning the numerical framework.

For example, in one experiment two different sets of solutions, the members of which contained the same concentrations to within experimental reproducibility, were made. In another experiment the same solution was measured, spectrophotometrically, three or four days later. The pertinent quantities were calculated for each of these cases and representative values given in Table 5.

The pattern is the same as before. For example two solutions of $C_2H_5NO_2$, having essentially the same degree of "fit" to Beer's Law, measured on the initial day of preparation, gave widely divergent

TABLE 5.—The Behavior of Pertinent Calculated Quantities for Selected Binary Solutions as a Function of Attempts at Chemical Reproducibility.

Solute	Solvent	Solution No.	Day of Measurement	$\lvert\overline{K}^{(1)}\rvert$ *l*/mole	$\overline{K}^{(1)}$ *l*/mole	Deviation (%)	$\overline{r}_1$	$\overline{r}_2$
CH_3NO_2	H_2O	1	1	676	338	187	.99538	.99447
	H_2O	2	1	861	—138	670	.99678	.99524
	H_2O	1	4	3800	—430	856	.99821	.99816
$C_2H_5NO_2$	H_2O	1	1	986	716	113	.99820	.99714
	H_2O	2	1	1410	80	1705	.99794	.99821
	H_2O	1	3	1490	—187	769	.99248	.98992

values of $K^{(1)}$ as shown by the average values. The correlation coefficients show some information of the nature of the chemistry; but, these, as usual, bear no relation to $K^{(1)}$ values.

Conclusion

The above results clearly show that, with the first iterate $K^{(1)}$, obtained from the iteration process given by de Maine, et al., (1957, 1960a), one cannot obtain a valid estimate of an association constant, K, if the chemical system obeys Beer's Law, (or nearly so). That is, if the deviations from Beer's Law are small, then there appears a complete randomness in the values of $K^{(1)}$.

On the other hand, the mathematical proof given in this paper shows that the starting point of the iterative procedure given by de Maine, et al., (1957, 1960a) is formally equivalent to an equation derived for a chemical system nearly obeying Beer's Law as a result of being composed almost entirely of dimer. Since a system which is nearly all dimer has a very large association constant ($K >> 1$), any value of $K^{(1)}$ which is small ($K^{(1)} < 1$) or large ($K^{(1)} > 1$) is questionable.

Since the binary solutions of nitroparaffins obey Beer's Law in the concentration ranges studied (Foley, et al., (1964)) the iteration process given by de Maine, et al., (1957, 1960a) does not give an interpretable value of $K^{(1)}$ because of randomness. It is possible that some chemical system exists which deviates significantly enough from Beer's Law to give a non-random value of $K^{(1)}$. However, since one could not iterate this value to a constant value (Musulin, et al., (1962)), and since the value is obtained from an equation which has no rigorous mathematical validity, the non-random $K^{(1)}$ could not be ascribed any reliability. Hence, one must conclude that the iterative procedure given by de Maine, et al., (1957, 1960a) has no practical value.

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