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Molecular Complexes

Part 18.[1]—A Nuclear Magnetic Resonance Adaptation of the Continuous Variation (Job) Method of Stoicheiometry Determination

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An n.m.r. counterpart of the classical Job method for determining the stoicheiometry of molecular complexes by spectrophotometry is derived. It is applied to the fluoranil–hexamethylbenzene and acetonitrile–benzene systems, for which stoicheiometries consistent with those deduced classically are obtained, although for the latter system an additional complex is identified. The method is used to reveal the dependence of the measured stoicheiometry on the solution concentration of the interacting species. It is demonstrated that 1 : 1 and 1 : 2 complexes can be identified separately when they coexist, and that the equilibrium constant for the formation of the former can be measured readily.

A continuing problem with n.m.r. studies of molecular complexes, particularly those formed transiently in solution, is the difficulty of establishing the stoicheiometry of the complexes.[2] To obtain information about the required stoicheiometries it is possible to use freezing point depression data[3] or conduct parallel spectrophotometric studies according to the continuous variation or Job method.[4] There appears, however, to be no unambiguous n.m.r. approach that can provide the relevant information. The intention here is to demonstrate how the Job method can be adapted simply for n.m.r. purposes.

Theoretical

If the stability of molecular complexes formed in solution is sufficiently high that resonances due to each of the species present can be observed, it is possible to study the complexes by intensity measurements for each of the absorptions. If, however, there is exchange of resonant species between various chemical sites the chemical shifts of the relevant species will be time-averaged. The following proposals are concerned with the use of time-averaged chemical shifts rather than intensities for continuous variation studies.[4]

The reaction of many species to form complexes amenable to study by n.m.r. can be represented by

$$A + nD = AD_n \quad (1)$$

where A and D often represent the acceptor and donor components of charge transfer complexes.

Consistent with Job's assumption, it is necessary to prepare solutions of A and D separately in the same solvent and at the same molarity M. A series of mixtures of the same total volume, V, must then be prepared from the two stock solutions, such that a fraction, x, of V is attributable to the solution of D. If c_A, c_D and c_{AD_n} are the equilibrium concentrations of A, D and AD_n, the expressions for these are given by

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$$c_A = M(1-x) - c_{AD_n} \quad (2)$$

$$c_D = Mx - nc_{AD_n} \quad (3)$$

$$c_{AD_n} = c_A c_D^n K \quad (4)$$

where eqn (4) derives from the ideal eqn (5),

$$K = (c_{AD_n}/c_A c_D^n)(\gamma_{AD_n}/\gamma_A \gamma_D^n). \quad (5)$$

Assuming that the solutions used are sufficiently dilute, the activity coefficient ratio in eqn (5) equates to unity. By appropriate manipulation of eqn (2)–(4) it can be confirmed[4, 5] that when

$$dc_{AD_n}/dx = 0 \quad (6)$$

$$n = x/(1-x). \quad (7)$$

The problem is to ascertain how this condition can be determined from n.m.r. studies.

Woldbye[6] has suggested that the conditions appropriate to eqn (7) can only be determined experimentally from measurements of the value, P, of a particular physical property of solutions if, and only if P is of the form

$$P = s_1[A] + s_2[D] + f[AD_n] \quad (8)$$

where s_1 and s_2 are constants. The normal procedure is to evaluate the difference, $\mathscr{Y}$, between the measured value of P and the value of P calculated under the assumption of no complex formation. Because $d\mathscr{Y}/dx$ is directly proportional to dc_{AD_n}/dx, a plot of $\mathscr{Y}$ against x shows a maximum or minimum when eqn (7) is valid.

In those circumstances when it is only possible to measure a time-averaged chemical shift this, according to the Gutowsky–Saika theory of fast exchange,[7] is given by

$$\delta_{obs} = f\delta_c + (1-f)\delta_{free} \quad (9)$$

where δ_{obs}, δ_{free} and δ_c are, respectively, the chemical shifts of the chosen species as observed in a particular mixture, of the uncomplexed species in that mixture and of the species in the complex, the amount of which contains a fraction, f, of the total amount of the species present initially. It is convenient to rearrange eqn (9) in terms of induced shifts as

$$\Delta_{obs} = f\Delta_c \quad (10)$$

where $f = c_{AD_n}/M(1-x)$. If a chemical shift for A is measured, it can be shown, by differentiating eqn (10) with respect to x, that

$$d\Delta_{obs}/dx = (dc_{AD_n}/dx)[\Delta_c/M(1-x)] + \Delta_{obs}/(1-x). \quad (11)$$

On the other hand, if a shift of D is measured, eqn (12) applies

$$d\Delta_{obs}/dx = (dc_{AD_n}/dx)(n\Delta_c/Mx) - \Delta_{obs}/x. \quad (12)$$

It can be seen from eqn (11) and (12) that a plot of the induced shift for neither A nor D against x can lead to either a maximum or minimum. However, it is possible to determine the value of x at which condition (7) holds. Inspection of eqn (11) reveals that when $dc_{AD_n}/dx = 0$ the slope of a plot of Δ_{obs} *versus* x will, at the appropriate value of x, be given by

$$d\Delta_{obs}/dx = \Delta_{obs}/(1-x). \quad (13)$$

It should be possible, therefore, to determine the value of x appropriate to eqn (7) and determine n. A similar treatment of eqn (12) reveals that the value of x appropriate to eqn (7) can be deduced from the condition

$$d\Delta_{obs}/dx = -\Delta_{obs}/x. \quad (14)$$

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Before implementing the approach described above it is prudent to assess the conditions under which experimental shifts realistically approximate to those required for the above equations.

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Experimental Conditions

It is well known that the shielding, σ, of a nucleus in the liquid phase is given by[8]

$$\sigma = \sigma_0 + \sigma_b + \sigma_w + \sigma_a + \sigma_E + \sigma_c \quad (15)$$

where the respective terms on the right-hand side of the equation refer to the shielding due to the isolated molecule in the gas phase, the volume magnetic susceptibility of the liquid, van der Waals forces between molecules, other magnetically anisotropic molecules, intermolecular electric fields and specific molecular interactions.

The shifts required for the approach outlined above can be measured relative to some reference compound. In this case the chemical shifts are due to the difference between two values given by eqn (15), one for A or D and the other for the reference. Alternatively, by using a spectrometer that is field/frequency locked to the resonance of a separate sample, it is possible to measure the resonance conditions appropriate to eqn (15) directly.

The advantage of using an internal reference compound is that it eliminates the effects of volume magnetic susceptibility and minimizes the effects of van der Waals, anisotropic and electric field origin.[9] A possible disadvantage may be that the addition of a fourth component, the reference, to the mixtures may be chemically undesirable. If the alternative method of measuring absolute resonance conditions is employed it is possible that all of the last five terms on the right-hand side of eqn (15) may vary with x. However, if the molarity of the solution, M, is very low the common solvent used for A and D will dominate the solvent screening effects, with the effects of A on D and *vice versa* being of little significance. For example, by choosing a suitably low value of M, and bearing in mind the fact that volume magnetic susceptibilities are additive on a volume fraction basis,[10] it is possible to keep variations in σ_b to a magnitude that is of the order of the error in the shift values; typically, therefore, M for organic systems might be < 0.1 mol dm^{-3}. Evidently it will also prove beneficial to choose an isotropic solvent to achieve these conditions, under which it can be deduced that σ_w and σ_E will also be approximately constant.[11, 12] Under these conditions similar arguments may be applied to the measurement of δ_{free}. Moreover, whether the shifts of A or D are studied, it may prove essential to prepare a separate reference solution for each value of x studied in which the concentration, of whichever of A or D is measured, is precisely the same as that in the mixture. The measured shifts for these solutions correspond to δ_{free} and when these are subtracted from the corresponding δ_{obs} to yield Δ_{obs}, not only will the gas phase shielding be eliminated, but variations in the other non-specific shielding terms will be further minimized.

Formation of 1:n and 1:$n+q$ Complexes

The foregoing proposals assume that only one complex is formed in solution. This assumption is often not valid and its failure is the base of one of the several criticisms[5, 6] of the continuous variation method. Whilst the extensive evaluation of analogous criticisms that may become apparent in the context of the present proposals is beyond the scope of this paper, it is prudent to examine the implications of two different complexes being formed according to

$$A + nD = AD_n + qD = AD_{n+q}. \quad (16)$$

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In this event, modifications must be made to the equations for the equilibrium concentrations of the various species present and these will cause changes to eqn (11) and (12). In order to illustrate this point it is convenient to consider the shift of A, the relevant equation for which is

$$\Delta_{obs} = c_{AD_n}\Delta_{AD_n}/(1-x)M + c_{AD_{n+q}}\Delta_{AD_{n+q}}/(1-x)M \quad (17)$$

from which it can be shown that

$$d\Delta_{obs}/dx = \Delta_{obs}/(1-x) + dc_{AD_n}/dx[\Delta_{AD_n}/(1-x)M] + dc_{AD_{n+q}}/dx[\Delta_{AD_{n+q}}/(1-x)M]. \quad (18)$$

From eqn (18) it can be seen that condition (13) can only be found when the last two terms of eqn (18) are equal and are of opposite sign. Some indication of the conditions at which this equality may be achieved may be obtained by considering the definitions of equilibrium concentrations appropriate to eqn (18). These reveal that

when $dc_{AD_n}/dx = 0$

$$dc_{AD_{n+q}}/dx = (c_A nM - c_D M)/[c_D + c_A n(n+q)]$$

and $$n = x/(1-x) + [(n+q)qc_{AD_{n+q}}]/[(1-x)M] \quad (19)$$

and when $dc_{AD_{n+q}}/dx = 0,$

$$dc_{AD_n}/dx = -Mqc_{AD_n}/(c_D - nqc_{AD_n})$$

and $$n = x/(1-x) - q - nqc_{AD_n}/M(1-x). \quad (20)$$

If these two conditions relate to maxima in the concentrations of the two complex species it is necessary, for the range of x between them or outside them, that the change in concentration of both complexes with x must be of opposite sign. Consequently, if Δ_{AD_n} and $\Delta_{AD_{n+q}}$ are of the same sign, the limits between which criterion (13) applies may be deduced. If $\Delta_{AD_n} \gg \Delta_{AD_{n+q}}$, dc_{AD_n}/dx can approach zero for the required condition to hold. Alternatively, if $\Delta_{AD_{n+q}} \gg \Delta_{AD_n}$, $dc_{AD_{n+q}}/dx$ can approach zero for condition (13) to apply. It follows from eqn (19) and (20) that condition (13) should be found at a value of x between limits somewhat below the value that would be found for the $1:n$ complex if formed alone and above that for the $1:n+q$ complex if it were formed alone. It is possible, for a system in which more than one complex is formed, that condition (13) may be found fortuitously at a value of x corresponding to the formation of a single complex only. In order to resolve this possible ambiguity the proposed method must be implemented for more than one value of M.

The Effect of M on the Significance of Induced Shifts

If A and D have suitable characteristics that facilitate, for example, the formation of a 1:2 complex, it is appropriate to enquire whether or not the choice of M influences the significance of the experimental shifts. It is interesting, therefore, to consider, at least qualitatively, the implications of the collisional mechanism for forming a 1:2 complex. If a 1:2 complex is formed this can arise in two ways. First, a 1:1 intermediate can be formed, but this must have a sufficiently long life-time that will enable it to undergo a subsequent collision with another molecule of D to form AD_2. At low concentrations of species forming relatively unstable complexes the probability of this occurring is low. Secondly, AD_2 may be formed by an appropriate termolecular collision, but again the probability of this happening at low concentrations is low. It is likely, therefore, that, unless the equilibrium constant for the formation of a $1:n$ complex is large, only 1:1 complexes will be formed at low values of M. Consequently, under these conditions it

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Table 1. Values of M for selected values of K for eqn (21) and (22) to apply

upper value of K /dm^3 mol^{-1}	upper limit to M /mol dm^{-3}
0.1	6
0.3	2
0.4	0.1
5	0.1
10	0.06
70	0.01

is probable that the induced shifts will, when analysed by the procedure outlined above (and by the classical spectrophotometric method?) indicate the presence of only a lower complex, possibly that of 1:1 stoicheiometry. It is essential, therefore, that continuous variation studies are carried out with at least two separated values of M.

Shapes of the Plots of Δ_{obs} *vs.* x

In anticipation of the possibility that 1:1 complex formation will be encountered frequently, it is worth considering what shape the plot of Δ_{obs} *vs.* x will have in this case.

If c_A and c_D in eqn (5), which is taken to be devoid of activity coefficients and for 1:1 complex formation, are substituted from eqn (2) and (3), it can be shown that f in eqn (10) is given by

$$f = KMx/(1+KM) \tag{21}$$

provided that c_{AD}^2 is equated to zero. Consequently, from eqn (10) it follows that the plot of Δ_{obs} *vs.* x could be linear. In these circumstances the slopes (S) of linear plots at different values of M can be used to deduce the equilibrium constant from

$$1/S = 1/KM\Delta_{AD} + 1/\Delta_{AD}. \tag{22}$$

The attraction of this is that K, and Δ_{AD}, could be determined over a range of M for which the stoicheiometry could be established. Consequently, it is important to note that eqn (21) and (22) only apply when

$$c_{AD}^2/M^2(1-x) \ll x. \tag{23}$$

Some of the experimental data presented later suggest that the left-hand side of eqn (23) need only be less than $0.1x$ for linear plots to be observed. However, it is probably wise to cautiously equate the limiting value to $0.05x$. Table 1 contains upper limits to M for selected values of K (obtained by numerical analysis) for which the plots of Δ_{obs} *vs.* x will be linear over the complete range of x.

For complexes other than 1:1, Δ_{obs} will depend on higher powers of x than 1 and the relevant plots will be curved.

In order to evaluate the above proposals the well studied[13, 14] system of fluoranil–hexamethylbenzene and that of acetonitrile–benzene[15] have been studied.

Experimental

The materials used were analytical grade or better. In the case of both systems, stock solutions of the compounds corresponding to A (hexamethylbenzene and acetonitrile) and D (fluoranil and benzene) were prepared gravimetrically to the same molarity. Initially, a molarity of 0.02 mol dm^{-3} was chosen for fluoranil–hexamethylbenzene in

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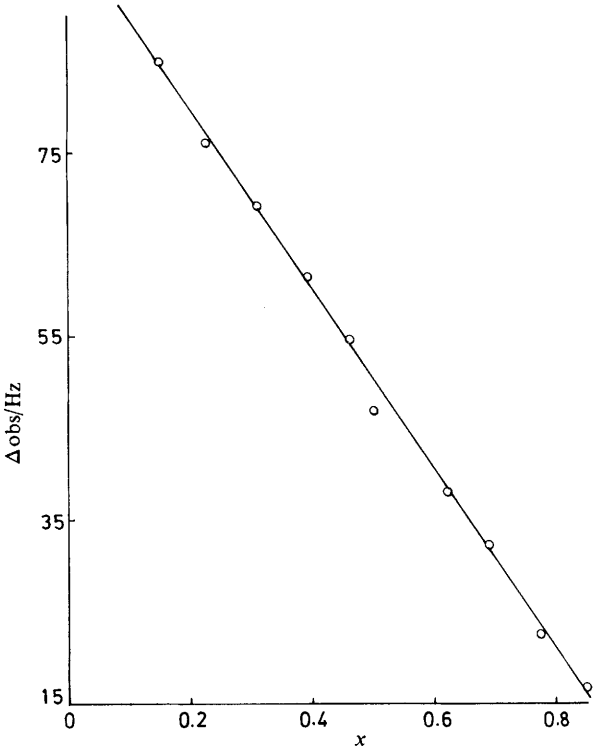

Fig. 1. Continuous variation plot for fluoranil–hexamethylbenzene; $M = 0.02$ mol dm^{-3} in CCl_4.

CCl_4 and for acetonitrile–benzene in CCl_4. As the induced shifts for this initial study of acetonitrile–benzene were found to be < 1 Hz the system was subsequently studied at 0.1 mol dm^{-3} and at higher concentrations in CCl_4. For each system, mixtures corresponding to a range of values of x were made to a fixed volume of 6.5 cm^3. At each value of x two samples were prepared, one to yield δ_{obs} and the other δ_{free}. The solutions were transferred using hypodermic syringes and injected *via* suba seals into the mixing vessels. The mixtures were sealed into 5 mm o.d. n.m.r. sample tubes. The ^{19}F chemical shifts of fluoranil were measured at 84.34 MHz and the ^{1}H shifts of acetonitrile were measured at 89.56 MHz using a field/frequency-locked (to external ^{7}Li) JEOL FX90Q pulsed Fourier-transform n.m.r. spectrometer operating at 25 °C; before investigation the samples were stored in a thermostatted bath, at the n.m.r. probe temperature, for at least one hour.

Results and Discussion

Fluoranil–Hexamethylbenzene

Fig. 1 presents the plot of the fluoranil ^{19}F shifts, Δ_{obs}, *vs.* x. The individual shifts were not internally referenced and derive from directly measured resonance frequencies that were not corrected for volume magnetic susceptibility because of the low value of M. The most striking feature of the plot is that the best fit line appears to be linear. As indicated earlier this in itself suggests that only a 1:1 complex is formed. The slope, S, of the line corresponds to eqn (14), and using this together with the appropriate intercept, I, enables the value of x corresponding to eqn (7) to be deduced from

$$x = -I/2S. \tag{24}$$

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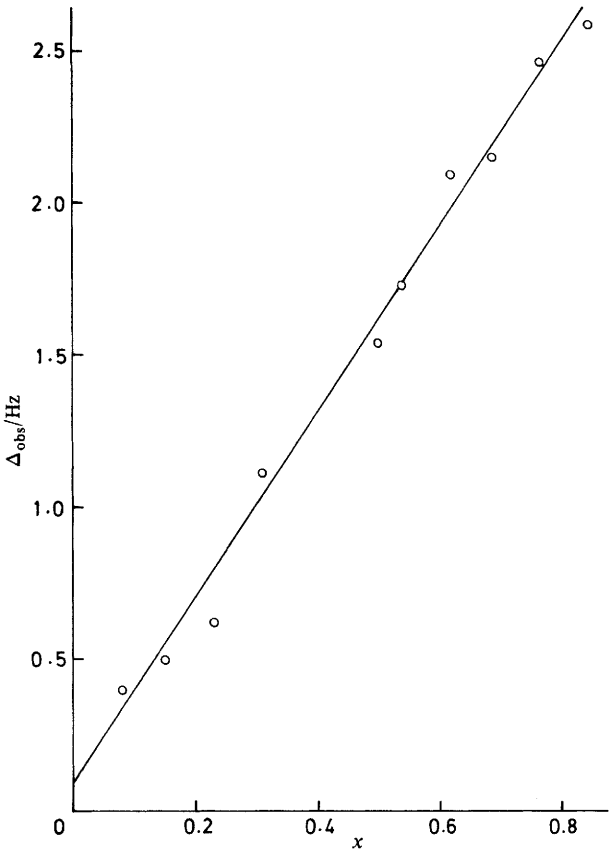

Fig. 2. Continuous variation plot for acetonitrile–benzene; $M = 0.1$ mol dm^{-3} in CCl_4.

This yields $x = 0.5$, which corresponds precisely with the value of $n = 1$ obtained by the spectrophotometric application of Job's method.[13] It should be noted that if the shifts of A are studied x should be obtained from

$$x = (S-I)/2S. \tag{25}$$

Acetonitrile–Benzene

Initially, this system was studied at 0.02 mol dm^{-3} in CCl_4, but no significant variation in the induced ^{1}H shifts of acetonitrile could be detected. The system was then investigated at 0.02 mol dm^{-3} in perdeuterocyclohexane. The deuterated compound was used in order to avoid potential problems arising from the overlap of proton resonances of the protonated analogue with that of acetonitrile. In this case small, but significant, induced shifts were observed and their variation with x appeared to be linear and this indicates that a complex of 1:1 stoicheiometry is formed. However, because, as mentioned earlier, the induced shifts are so small the above conclusion could be open to question. Consequently, the system was re-investigated at 0.1 mol dm^{-3} in CCl_4. The relevant plot is shown in fig. 2 which again indicates the formation of a 1:1 complex. This is particularly surprising because Polanun[15] has shown by very careful cryoscopic experiments that a 1:2 complex is formed. This leads to speculation on the suggestions made earlier that the choice of M may influence the origin of the induced shifts and that

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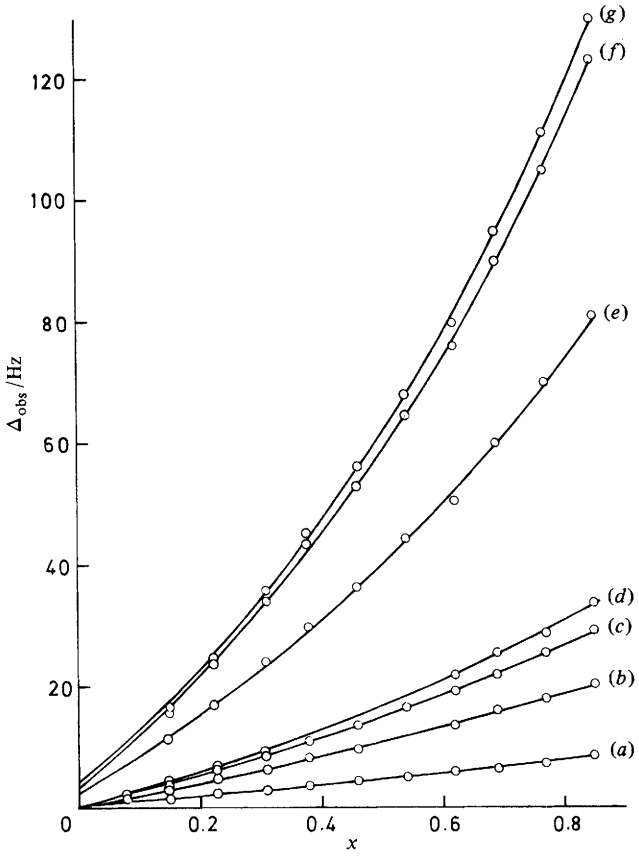

Fig. 3. Continuous variation plots for acetonitrile–benzene: M in the range 0.4–11 mol dm^{-3}. (*a*) 0.4; (*b*) 1.0; (*c*) 1.6; (*d*) 2.0; (*e*) 6.0; (*f*) 11.0; (*g*) 11.0 (3 °C) mol dm^{-3}.

at low values of M only a 1:1 complex may be detected. Bearing these points in mind the acetonitrile–benezene system was re-investigated at values of M up to 11 in CCl_4. The shifts in each case were measured absolutely and corrected for volume magnetic susceptibility on a volume fraction basis. The values of χ were deduced from the density and specific susceptibilities given in ref. (16) and (17), respectively. The data are presented in fig. 3. The plots in each case are non-linear and this suggests that a 1:1 complex is not present alone.

It can be seen from fig. 3 that the curvature of the plots increases with M. Each set of data was fitted to the polynomial of the lowest degree that yielded the most satisfactory intercept on the Δ_{obs} axis. It should be noted that this was not always zero. This could be due either to residual solvent effects or to the fact that two or more complexes co-exist. The polynomial equations were subject to further computer analyses to establish the values of x at which condition (13) applies. The values of x so found lie in the range 0.51–0.59. From the earlier discussion of the effect of the presence of two complexes on the value of x deduced from condition (13) it would appear that both 1:1 and 1:2 complexes coexist in the acetonitrile–benzene systems studied here. This conclusion was confirmed in the following manner.

At very small values of x the probability of 1:2 complexes contributing to the measured values of Δ_{obs} must be small. Consequently, the initial slopes of the Δ_{obs} *vs.* x plots may be taken to reflect the contribution to Δ_{obs} of the dominant 1:1 complex in the presence

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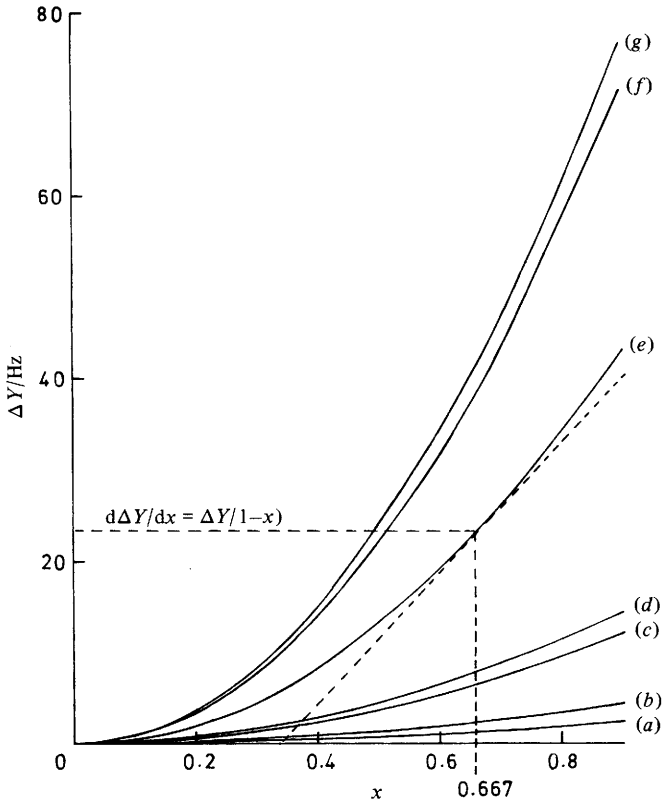

Fig. 4. Corrected continuous variation plots for acetonitrile–benzene; for definition of Y see text. (*a*)–(*g*) as in fig. 3.

of the smaller amount of 1:2 complex. The linear equations corresponding to the initial slopes can be used to correct the experimental values of Δ_{obs} and produce plots of Δ_{obs}, now labelled Y, *vs.* x that reflect the effect of the second complex alone over the complete range of x. The relevant data are shown in fig. 4. Iterative computer analyses of each plot to establish when $dY/dx = Y/(1-x)$ revealed that in each case this occurred at $x = 0.667$. Because c_{AD_n} in eqn (20) has been effectively set equal to zero it follows that $n+q = 2$ and a 1:2 complex was detected. This is consistent with the finding of Polanun[15] who presumably only identified a complex of this stoicheiometry because his cryoscopic studies were on binary mixtures of the interacting species at effectively high concentration and low temperature when the 1:2 complex would dominate the 1:1. In order to investigate qualitatively the effect of temperature on the relative amounts of 1:1 and 1:2 complexes the 11 mol dm^{-3} system was studied at 3 °C. The results are shown in fig. 3 and 4. From the former the higher value of x at which condition (13) is found and from the latter the increased curvature both indicate that a reduction in temperature favours the formation of the 1:2 over the 1:1 complex.

The overall consistency of the immediately foregoing treatment of the experimental data appears to justify the underlying assumptions. It follows that the initial slopes of the plots in fig. 3 should be amenable to evaluation using eqn (22). Fig. 5 shows the appropriate plot from which a value of $K_{1:1} = 0.27$ dm^3 mol^{-1} may be obtained. Although there is no reference value for comparison it is worth noting that concurrent investigations[18] on quite different systems show that eqn (22) and a conventional Benesi–Hildebrand[19] study yield alniost identical values for $K_{1:1}$.

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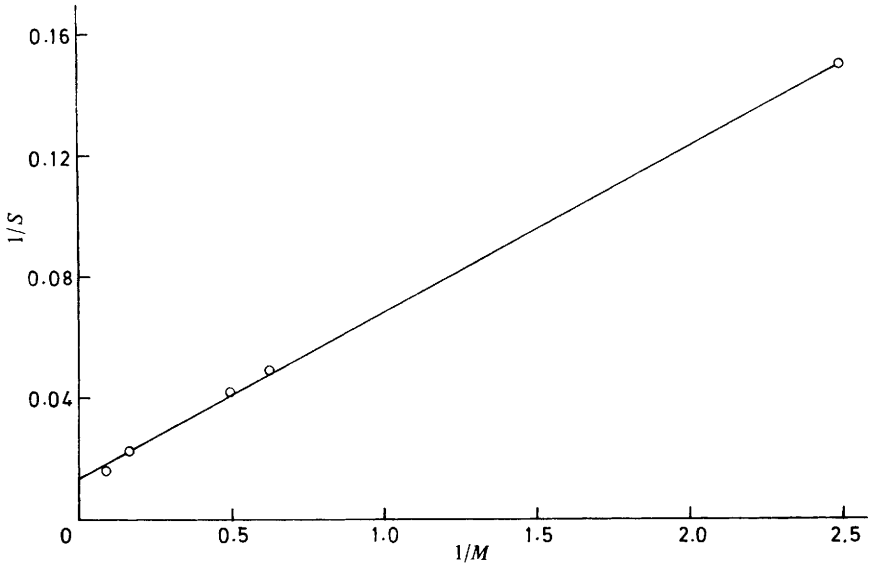

Fig. 5. $1/S$ *vs.* $1/M$ plot relating to eqn (22) for acetonitrile–benzene.

Conclusions

Although the limitations of the proposals presented here need to be evaluated fully, it does appear from preliminary investigations that the n.m.r. analogue of the Job or continuous variation method affords a sensitive method of determining the stoicheiometries of complexes formed in solution. Of particular interest is the fact that it is possible to comment on whether one or more complexes are present and in the specific case of the co-existence of 1:1 and 1:2 complexes it is possible to identify both. When 1:1 complexes can be identified it is possible to determine the equilibrium constants for their formation from the same experiments that confirm their existence. The method has a significant advantage over its spectrophotometric analogue in that it does not require the complexes formed to show a charge-transfer band or in a wider sense be 'coloured'.

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References

1 J. Homer and A. Coupland, *J. Chem. Soc., Faraday Trans. 2*, 1978, **74**, 2187.
2 See *e.g.*, J. Homer and M. C. Cooke, *J. Chem. Soc. A*, 1969, 773, references therein and other Parts in this series.
3 L. W. Reeves and W. G. Schneider, *Can. J. Chem.*, 1957, **35**, 251.
4 P. Job, *C. R. Acad. Sci.*, 1925, **180**, 928; *Ann. Chim.*, 1928, **9**, 113.
5 W. C. Vosburgh, and G. R. Cooper, *J. Am. Chem. Soc.*, 1941, **63**, 437.
6 F. Woldbye, *Acta Chem. Scand.*, 1955, **9**, 299.
7 H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, 1953, **21**, 1688.
8 A. D. Buckingham, T. Schaefer and W. G. Schneider, *J. Phys. Chem.*, 1960, **32**, 1227.
9 See *e.g.*, J. Homer, *Appl. Spectrosc. Rev.*, 1975, **9**, 1.
10 See *e.g.*, J. A. Pople, W. G. Schneider and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance* (McGraw-Hill, London, 1959).
11 J. Homer and C. C. Percival, *J. Chem. Soc., Faraday Trans. 2*, 1984, **80**, 1.
12 A. D. Buckingham, *Can. J. Chem.*, 1960, **38**, 300.

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13 B. Dodson, R. Foster and A. A. S. Bright, *J. Chem. Soc. B*, 1971, 1283.
14 R. Foster and D. R. Twiselton, *Recl. Trav. Chim.*, 1970, **89**, 1211.
15 P. Polanun, *Ph.D. Thesis* (The University of Aston in Birmingham, 1973).
16 J. Timmermans, *Physico-chemical Constants of Pure Organic Compounds* (Elsevier, Amsterdam, 1965).
17 *Handbook of Chemistry and Physics*, ed. R. Weast (Chemical Rubber Co., Florida, 57th edn, 1976).
18 J. Homer, M. M. Ayad and R. M. Issa, unpublished results.
19 H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703.

Paper 5/882; *Received* 28*th May*, 1985

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