

Graphic Method for the Determination of the Complex NMR Shift and Equilibrium Constant for a Hetero-association accompanying a Self-association

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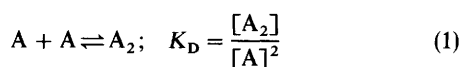
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A novel graphic method to determine the complex shift and equilibrium constant for a hetero-association, $A + B \rightleftharpoons AB$, accompanying a self-association $A + A \rightleftharpoons A_2$ has been described. The method is to be used in conjunction with a graphic determination of the monomer shift, dimer shift and dimerization constant proposed previously. Our new method is advantageous over the conventional Benesi–Hildebrand (BH) plot in that the limitations, (1) that the concentration of one component must be much less than that of the other and (2) that self-association of species is not allowed, are completely removed. The related parameters of the self-association of 2-isopropylphenol (A) and the hetero-association of 2-isopropylphenol with acetone (B) in the inert solvent $[^2H_{1,2}]$ cyclohexane has been used to demonstrate the use of this new graphic method. Comparison with the results from a BH plot has also been made.

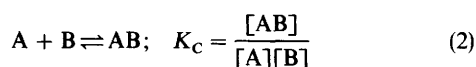
Molecular association due to hydrogen bonding or electron donor–electron acceptor charge transfer has long been of interest to chemists.^{1–4} It has been investigated by a variety of experimental and theoretical means.^{5–7} The traditional approach to derive the spectroscopic parameters and equilibrium constant from the experimental data (UV or NMR) was pioneered by Benesi and Hildebrand (BH).⁸ However, the conventional BH plot or its modifications, Scatchard⁹ and Scott¹⁰ plots, are subject to the limitation that the concentration of one component is much less than that of the other. Another restriction is also implied, although not explicitly expressed, that the self-association of species is not allowed. These limitations have immediate consequences (1) the monitored signal may be too weak to be observed, (2) there may be an extended association beyond AB, such as AB_2 , AB_3 etc., (3) the solution is thermodynamically non-ideal so that activity, instead of concentration, should be used in the equilibrium constant expression. These limitations undoubtedly lead to an erroneous determination of the spectroscopic parameters and equilibrium constant. Thus, the subsequent determination of ΔH and ΔS derived from a van't Hoff plot is not reliable. In this paper we propose a novel algorithm to determine the complex shift and equilibrium constant for a hetero-association accompanying a self-association in an inert solvent. The limitations imposed by the BH approach are completely removed in this new algorithm.

Theory

Consider a system containing species A and B in an inert solvent in which dimerization of A



and a hetero-association of A and B



are taking place simultaneously. Here $[A]$, $[A_2]$ and $[AB]$ are the equilibrium concentrations of monomer A, dimer A_2 and complex AB, respectively. K_D and K_C are the equilibrium constants for dimerization and hetero-association,

respectively. Consideration of mass balance results in

$$[A]_0 = [A] + [AB] + 2[A_2] \quad (3)$$

$$[B]_0 = [B] + [AB] \quad (4)$$

where $[A]_0$ and $[B]_0$ are the initial concentration of A and B.

Substituting eqn. (4) into eqn. (2) and solving for $[AB]$, one obtains

$$[AB] = [B]_0 \frac{K_C[A]}{1 + K_C[A]} \quad (5)$$

Further substitutions of eqn. (1) for $[A_2]$ and eqn. (5) for $[AB]$ into eqn. (3) gives a cubic equation for $[A]$ after rearrangement:

$$2K_D K_C [A]^3 + (2K_D + K_C)[A]^2 + (1 + K_C[B]_0 - K_C[A]_0)[A] - [A]_0 = 0 \quad (6)$$

Hence, if K_C and K_D are known, a pair of initial concentrations $[A]_0$ and $[B]_0$ permits us to solve for $[A]$. Although mathematically there are three roots for eqn. (6), physically $[A]$ is to be between 0 and $[A]_0$. We can rewrite eqn. (6) as

$$f(x) = 2K_D K_C x^3 + (2K_D + K_C)x^2 + (1 + K_C[B]_0 - K_C[A]_0)x - [A]_0 = 0 \quad (7)$$

According to the Descartes' rule of signs,¹¹ the number of positive roots of a polynomial equation is equal to the number of variations in signs of the coefficients, or this number decreases by an even integer. In eqn. (7), the coefficients of cubic and quadratic terms are positive, while that of the constant term is negative. Thus, there is only one change in sign, no matter what the sign of the coefficient of the linear term. Since a negative root is unphysical, there is only one positive root. Moreover, with $f([A]_0) = 2K_D K_C [A]_0^3 + 2K_D [A]_0^2 + K_C [A]_0 [B]_0 > 0$, and $f(0) = -[A]_0 < 0$, it can be asserted that this positive root lies between 0 and $[A]_0$.

In NMR measurements, the observed chemical shift for a nucleus in A, which involves rapid dimerization and hetero-association, is the weighted average of the shift contributed from the monomer A, dimer A_2 and complex AB, with their respective mole fractions, f_A , f_D , f_C , as the weight factors.

According to Gutowsky and Saika,¹² we have

$$\Delta v_{\text{obs}} = f_A \Delta v_A + f_D \Delta v_D + f_C \Delta v_C \quad (8)$$

where Δv_A , Δv_D , Δv_C are the chemical shifts of A, A₂, and AB. The various mole fractions are expressed as

$$f_A = [A]/[A]_0 \quad (9)$$

$$f_D = [A_2]/[A]_0 = K_D [A]^2/[A]_0 \quad (10)$$

$$f_C = \frac{[AB]}{[A]_0} = \frac{[B]_0}{[A]_0} \frac{K_C [A]}{1 + K_C [A]} \quad (11)$$

where eqn. (5) has been used in eqn. (11).

To proceed, define

$$\Delta v^* = f_C \Delta v_C = \Delta v_{\text{obs}} - f_A \Delta v_A - f_D \Delta v_D \quad (12)$$

The last equality is due to eqn. (8). With eqn. (11), eqn. (12) becomes

$$\Delta v^* = \frac{[B]_0}{[A]_0} \frac{K_C [A]}{1 + K_C [A]} \Delta v_C \quad (13)$$

which can be rearranged to

$$\frac{[B]_0}{[A]_0} \frac{1}{\Delta v^*} = \frac{1}{\Delta v_C} + \frac{1}{\Delta v_C K_C} \frac{1}{[A]} \quad (14)$$

A plot of the left-hand side of eqn. (14) vs. $1/[A]$ permits us to derive Δv_C and K_C from the intercept and slope. However, to calculate $[A]$ we need to know K_D and K_C ; to calculate Δv^* we need to know Δv_A and Δv_D . The graphic method for the determination of Δv_A , Δv_D and K_D from the dilution shift data of a self-association has been published elsewhere,^{13–15} and will be presented briefly in the following section.

Proposed Algorithm

Self-association

For a system with self-association, two physically equivalent equations expressing the observed chemical shift as a function of solute concentration have been derived:^{13–15}

$$\Delta v_{\text{obs}} = \Delta v_D - \left(\frac{\Delta v_D - \Delta v_A}{2K_D} \right)^{1/2} \left(\frac{\Delta v_{\text{obs}} - \Delta v_A}{[A]_0} \right)^{1/2} \quad (15)$$

$$\Delta v_{\text{obs}} = \Delta v_A + (\Delta v_D - \Delta v_A) \frac{(1 + 8K_D[A]_0)^{1/2} - 1}{(1 + 8K_D[A]_0)^{1/2} + 1} \quad (16)$$

In the previous study, an iteration scheme was used to determine Δv_A , Δv_D and K_D from the dilution shift data of a self-association system. Based on eqn. (15) a guessed value of Δv_A is inserted into $X = (\Delta v_{\text{obs}} - \Delta v_A/[A]_0)^{1/2}$, followed by regression of the data of Δv_{obs} vs. X using a quadratic (instead of a linear) equation to calculate tentative values of Δv_D and K_D from the intercept and limiting slope (*i.e.* slope at $X = 0$) of the regressed curve. K_D thus obtained is then inserted into f_D , followed by regression of the data of Δv_{obs} vs. f_D based on eqn. (16) again using a quadratic equation to obtain Δv_A from the intercept of the regressed curve. Thus, the first iteration is completed. The newly obtained Δv_A is then inserted into X to start the second iteration to obtain a further improved value of K_D , which in turn is used to obtain a better value of Δv_A . The interaction procedure is repeated until the difference of two successive values of Δv_A is less than a pre-set tolerance.

We propose here another more effective and accurate graphic method. The preliminary result has been published elsewhere.¹⁴ The crucial ideal behind this graphic method lies in the fact that, if a correct value of Δv_A in X is guessed to

regress the data of Δv_{obs} vs. X , the regressed curves will be identical irrespective of whether linear or quadratic equations are used. Hence, in this special case, a pair of 'true' values of Δv_D and K_D can be derived from the intercept and slope of the regressed linear curve. If, on the other hand, an incorrect value of Δv_A in X is guessed, the regressed curves corresponding to linear and quadratic equations will be different. As a result, regressed values of Δv_D from the intercept, and K_D from the slope (limiting slope if a quadratic equation is used) for the linear and quadratic regressions will correspondingly be different. One might take the advantage of this fact to find the correct values of Δv_A and K_D by the following strategy: Plotting regressed values of K_D vs. guessed value of Δv_A , from linear and quadratic regressions results in two curves. The determined 'true' values of Δv_A and K_D based on eqn. (15) are then found from the intersection, since only at this point do both regressions have the same values of Δv_A and K_D , which correspond to the 'true' values.

By the same token, based on eqn. (16), inserting a guessed value of K_D into $f_D = [(1 + 8K_D[A]_0)^{1/2} - 1]/[(1 + 8K_D[A]_0)^{1/2} + 1]$, followed by regressing the data of Δv_{obs} vs. f_D using linear and quadratic polynomials gives two regressed values of Δv_A from the intercepts. Again, a correct value of K_D results in the same regressed values of Δv_A , irrespective of whether linear or quadratic polynomials are used. Δv_A and K_D , based on eqn. (16), can then be determined from the intersection of two separate curves plotted for guessed values of K_D vs. regressed values of Δv_A .

Theoretically, the results based on either eqn. (15) or eqn. (16) are expected to be identical, since they represent the same pair of to-be-determined Δv_A and K_D . Any difference in these values, however, may reflect (1) the experimental error of shift and/or solute concentration measurement; (2) extended association beyond dimerization, and (3) the non-ideal thermodynamic behaviour of the solution. The last possibility arises from the fact that the equilibrium constant depends on the solute concentration in a non-ideal thermodynamic solution. This behaviour is inconsistent with the underlying assumption that the equilibrium constant should be a constant value throughout the concentration range studied. Without bias to either determination, we treat both of them on an equal footing. As a result, the average of Δv_A (or K_D) from two determinations is taken as the finally determined value of Δv_A (or K_D). The finally determined value of Δv_A is then inserted into X followed by linear regression on the data of Δv_{obs} vs. X to obtain a regressed value of Δv_D based on eqn. (15) from the intercept. Similarly, the finally determined value of K_D is inserted into f_D , followed by linear regression on the data of Δv_{obs} vs. f_D to obtain the regressed values of Δv_D based on eqn. (16) from the intercept at $f_D = 1$. The average of Δv_D from these two results is then taken as the finally determined value of Δv_D .

Hetero-association

Eqn. (14) is that on which the algorithm for obtaining Δv_C and K_C is based. If K_D has been already determined, with a guessed value of K_C , one can solve eqn. (6), at least numerically, for $0 < [A] < [A]_0$ from a pair of initial concentrations of $[A]_0$ and $[B]_0$. The value of $[A]$ thus obtained is then used to calculate f_A in eqn. (9), and f_D in eqn. (10). Δv^* in eqn. (12) is then readily calculated if the parameters Δv_A and Δv_D have also been determined. A linear regression on the data of $[B]_0/[A]_0 \Delta v^*$ vs. $1/[A]$ based on eqn. (14) then gives the regressed values of Δv_C and K_C from the intercept and slope. If the K_C is correctly guessed, the regressed value and guessed value of K_C will be the same, otherwise they are different. The correct, finally determined value of K_C may be obtained from

the intersection of a plot for y (= regressed values of K_C) vs. x (= guessed values of K_C) and another one for $x = y$. The last plot is just an artifice to locate the point where K_C has the same guessed and regressed values. The regressed value of $\Delta\nu_C$ obtained from the intercept of the linear plot of $[B]_0/([A]_0\Delta\nu^*)$ vs. $1/[A]$ by using the finally determined value of K_C is then taken as the finally determined value of $\Delta\nu_C$.

Experimental

We have carried out an NMR study of a self-association system of 2-isopropylphenol (A) in $[^2H_{12}]$ cyclohexane and another on a system where the self-association of A and the hetero-association between A and acetone (B) take place simultaneously in $[^2H_{12}]$ cyclohexane. The 300 MHz proton spectra were recorded on a Varian Unity-300 NMR spectrometer at 25 °C. All chemicals were the highest purity grade from Aldrich and used as received. Samples of different concentrations, containing a trace of TMS as a reference, were prepared. The samples of known concentration were then transferred into 5 mm od MNR tubes, and were sealed without further degassing.

The peak of the hydroxy group in 2-isopropylphenol was used to monitor the change of shift with concentration. All the data manipulation and graphic plotting are performed by programs written in the language of *Mathematica*.¹⁶

Results and Discussion

Somers and Gutowsky¹⁷ have investigated the self-association of 2-isopropylphenol in CCl_4 using the NMR dilution shift. They obtained a dimerization constant of $1.7 \text{ dm}^3 \text{ mol}^{-1}$. They concluded that 2-isopropylphenol undergoes monomer-dimer equilibrium because the bulky isopropyl group prevents further aggregation such as trimerization or tetramerization. We will also assume the self-association for 2-isopropylphenol in cyclohexane to be substantially limited to dimerization. The system is hence chosen to test the validity of our newly proposed graphic method.

Fig. 1 represents a graphic determination of $\Delta\nu_A$ and K_D from the dilution shift data of 2-isopropylphenol in $[^2H_6]$ cyclohexane at 25 °C as listed in Table 1. The curves L1 and Q1 represent the plots for regressed values of K_D vs. guessed values of $\Delta\nu_A$, for linear and quadratic regressions respectively, based on eqn. (15). The curves L2 and Q2 rep-

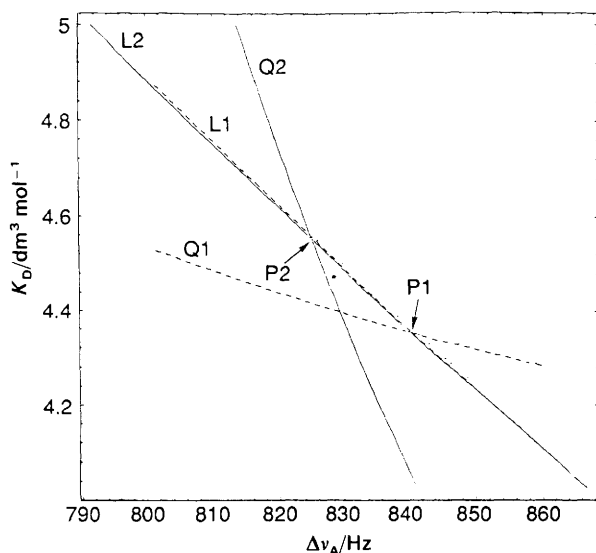


Fig. 1 Graphic determination of $\Delta\nu_A$ and K_D of 2-isopropylphenol in $[^2H_{12}]$ cyclohexane at 25 °C

Table 1 Dilution shifts of 2-isopropylphenol in $[^2H_{12}]$ cyclohexane and the finally determined values of $\Delta\nu_A$, $\Delta\nu_D$ and K_A at 25 °C

concentration/mol dm^{-3}	$\Delta\nu_{\text{obs}}/\text{Hz}$
0.2178	1377.45
0.3263	1442.73
0.4680	1505.31
0.5799	1535.72
0.7305	1573.27
0.9206	1608.26
1.2341	1645.95
1.5247	1670.44
1.9469	1696.41
2.7518	1726.97
3.7367	1748.10
finally determined values:	$\Delta\nu_A = 832.50 \text{ Hz}$
	$\Delta\nu_D = 1926.82 \text{ Hz}$
	$K_D = 4.46 \text{ dm}^3 \text{ mol}^{-1}$

resent the plots of guessed values of K_D vs. regressed values of $\Delta\nu_A$, for linear and quadratic regressions, respectively, based on eqn. (16). Note that L1 and L2 almost coincide. The intersection P1 from L1 and Q1 then determines the values of $\Delta\nu_A$ and K_D based on eqn. (15), while P2 from L2 and Q2 determines those based on eqn. (16). Ideally P1 and P2 are expected to coincide. The departure reflects the non-ideal conditions discussed above. With P1 and P2, the finally determined values of self-association parameters are then determined to be $\Delta\nu_A = 832.50 \text{ Hz}$, $\Delta\nu_D = 1926.70 \text{ Hz}$, $K_D = 4.46 \text{ dm}^3 \text{ mol}^{-1}$. These values are used in the subsequent determination of K_C and $\Delta\nu_C$, and are also included in Table 1.

As shown in Fig. 2, the determination is assessed by checking the agreement between the theoretical plot of $\Delta\nu_{\text{obs}}$ vs. X based on eqn. (15) calculated from the finally determined values of the parameters and the points calculated from the experimental data. Similar plots for $\Delta\nu_{\text{obs}}$ vs. f_D based on eqn. (16) and $\Delta\nu_{\text{obs}}$ vs. $[A]_0$ are also presented in Fig. 3 and 4.

Once $\Delta\nu_A$, $\Delta\nu_D$ and K_D have been determined, we are in a position to determine $\Delta\nu_C$ and K_C from the data of $\Delta\nu_{\text{obs}}$ vs. $[B]_0$ at constant concentration of A as listed in Table 2. Fig. 5 represents the graphic determination of K_C based on eqn. (14). We have found the finally determined value of K_C to be

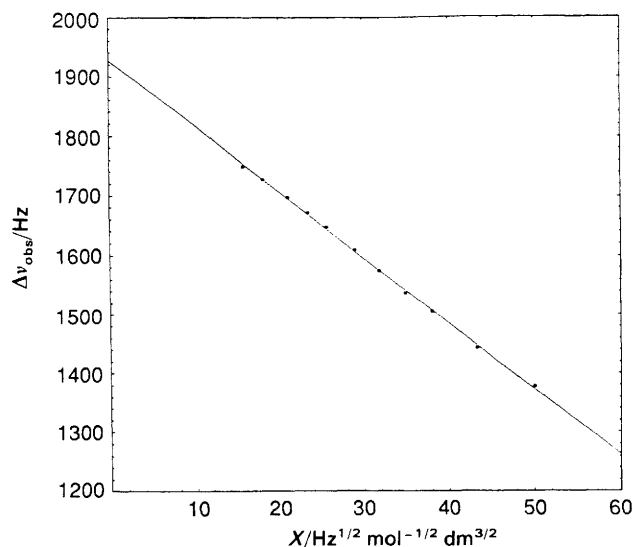


Fig. 2 Plot for $\Delta\nu_{\text{obs}}$ vs. X for an assessment of the determination of $\Delta\nu_A$, $\Delta\nu_D$ and K_D from Fig. 1 for 2-isopropylphenol in $[^2H_{12}]$ cyclohexane

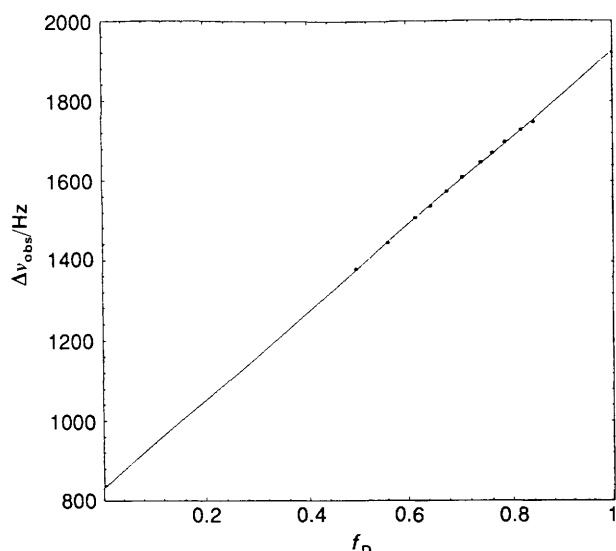


Fig. 3 Plot for Δv_{obs} vs. f_D for an assessment of the determination of Δv_A , Δv_D and K_D from Fig. 1 for 2-isopropylphenol in $[^2\text{H}_{12}]\text{cyclohexane}$

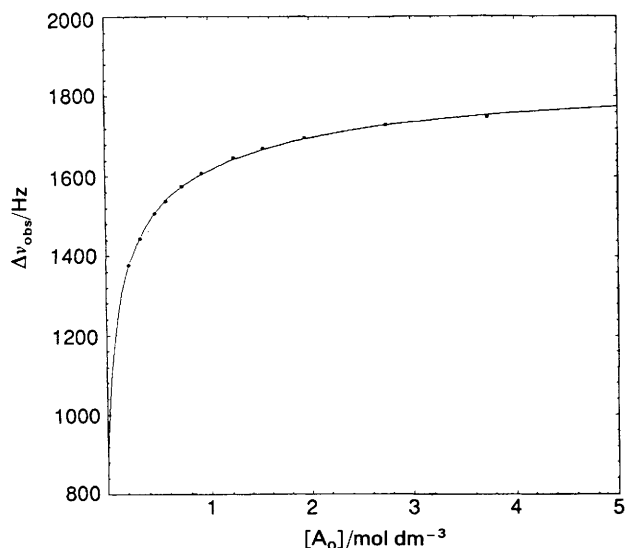


Fig. 4 Plot for Δv_{obs} vs. $[A]_0$ for an assessment of the determinations of Δv_A , Δv_D and K_D from Fig. 1 for 2-isopropylphenol in $[^2\text{H}_{12}]\text{cyclohexane}$

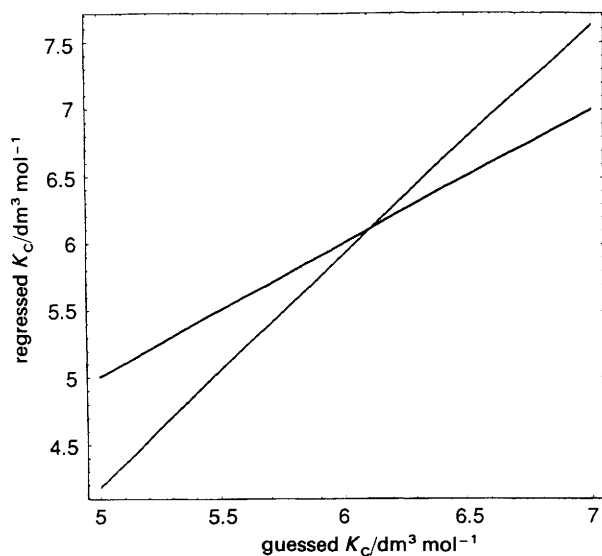


Fig. 5 Graphic determination of K_C based on eqn. (14)

Table 2 Dilution shifts for 0.1946 mol dm⁻³ 2-isopropylphenol association with acetone at various concentrations in $[^2\text{H}_{12}]\text{cyclohexane}$ at 25 °C

concentration/mol dm ⁻³	$\Delta v_{\text{obs}}/\text{Hz}$
0	1349.13
0.6439	1976.40
0.8250	2082.84
1.1521	2174.17
1.5152	2219.72
1.7873	2246.81
2.0211	2261.71
2.5043	2287.54
2.7104	2294.64
2.8225	2297.30
3.3615	2313.67
3.3789	2312.06
3.4919	2314.04
3.6606	2318.18
4.1261	2326.70
4.5425	2333.82

finally determined values:	$\Delta v_C = 2390.92 \text{ Hz}$ $K_C = 6.11 \text{ dm}^3 \text{ mol}^{-1}$
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6.11 dm³ mol⁻¹. Fig. 6 shows the linear plot of the theoretical curve of $[B]_0/([A]_0 \Delta v^*)$ vs. $1/[A]$ calculated from the determined parameters Δv_A , Δv_D , K_D and K_C . From the intercept Δv_C is found to be 2390.92 Hz. It is also found that the theoretical plot agrees fairly well with the points calculated from the experimental data.

As pointed out earlier, the conventional BH method assumes $[B]_0 \gg [A]_0$ and ignores the possibility of self-association. These two limitations are completely removed in our newly proposed graphic method. It is interesting to compare the result from our method to that from BH. The BH equation reads:

$$\frac{1}{\Delta v_{\text{obs}} - \Delta v^*} = \frac{1}{\Delta v_C - \Delta v^*} + \frac{1}{(\Delta v_C - \Delta v^*)K_C} \frac{1}{[B]_0} \quad (17)$$

where Δv^* is the chemical shift of monomer A, which has been previously determined to be 832.50 Hz. If we assume there is no self-association for A, the observed shift of 1349.13

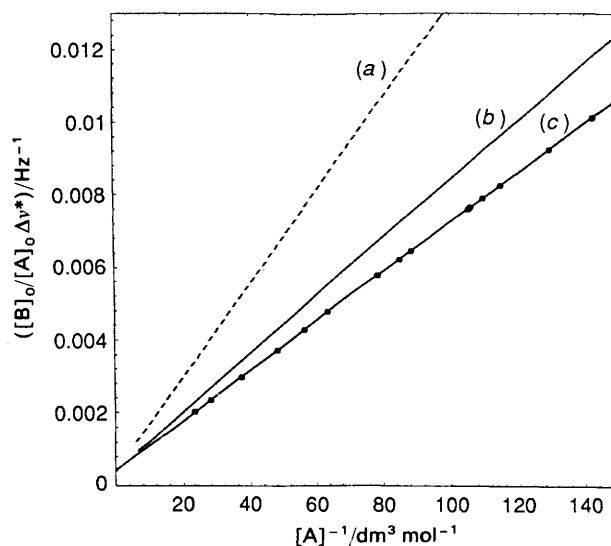


Fig. 6 Plots of $[B]_0/([A]_0 \Delta v^*)$ vs. $1/[A]$ for experimental data and theoretical curves calculated from various determinations: (a) BH with $\Delta v^* = 1349.13 \text{ Hz}$; (b) BH with $\Delta v^* = 832.50 \text{ Hz}$; (c) our method

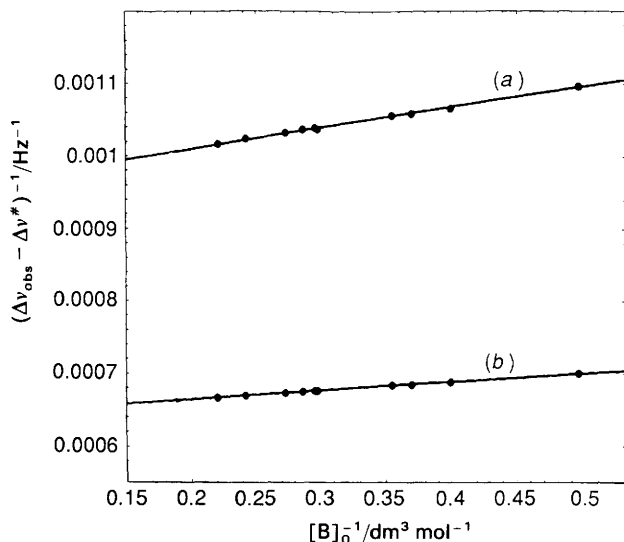


Fig. 7 BH plots for the determination of Δv_C and K_C : (a) $\Delta v^* = 1349.13$ Hz; (b) $\Delta v^* = 832.50$ Hz

Hz for $[A]_0 = 0.1964$ mol dm^{-3} in the absence of B can be used. Since the BH plot requires $[B]_0 \gg [A]_0$, we have only chosen in Table 2 the portion of the data where $[B]_0$ is equal to or greater than 2.0211 mol dm^{-3} . The determination using the BH plot is shown in Fig. 7. For $\Delta v^* = 832.50$ Hz we have found $\Delta v_C = 2397.58$ Hz and $K_C = 5.20$ $\text{dm}^3 \text{mol}^{-1}$; while for $\Delta v^* = 1349.13$ Hz we have found $\Delta v_C = 2400.79$ Hz and $K_C = 3.26$ $\text{dm}^3 \text{mol}^{-1}$. There is considerable disparity for three determinations on K_C but not for Δv_C . In Fig. 6, plots of $[B]_0/([A]_0 \Delta v^*)$ vs. $1/[A]$ for two BH determinations are also juxtaposed with that same plot for our determination for comparison. Since in the BH method no self-association is

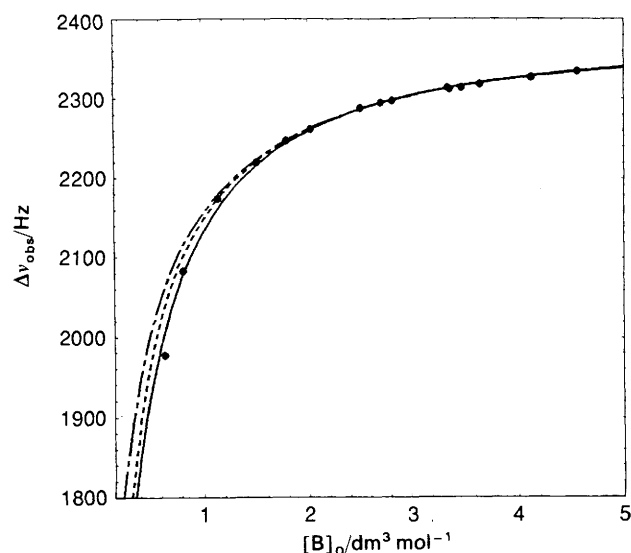


Fig. 8 Plot for Δv_{obs} vs. initial concentration of acetone for an assessment of various determinations of Δv_C and K_C : (—) our method; (----) BH with $\Delta v^* = 832.50$ Hz; (-.-.-) BH with $\Delta v^* = 1349.13$ Hz

allowed, $[A]$ can be obtained by solving eqn. (6) with $K_D = 0$. Δv^* in BH determination is, however, calculated from $f_C \Delta v_C$, where f_C in turn is calculated from eqn. (11). It is found that the plot based on eqn. (14) gives a very good criterion for the merits of the various determinations. On the other hand, the plot of Δv_{obs} vs. $[B]_0$ fails to do so, as can be seen from Fig. 8.

Conclusion

In conjunction with the graphic method for the determination of Δv_A , Δv_D and K_D from the dilution shift data for the self-association of A, we have proposed a new algorithm which enables us to determine the values of Δv_C and K_C for a hetero-association accompanying a self-association. Our method is superior to the conventional BH method as the limitation of the assumption $[A]_0 \ll [B]_0$ is removed, and the possibility of the self-association of A is taken into account. With a practical example of 2-isopropylphenol and acetone in cyclohexane we have demonstrated that the new algorithm gives better results than the BH method. We believe, our new algorithm will lend itself to a reliable thermodynamic studies of association systems by NMR or other spectroscopic means.

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