Molecular Complexes. Preliminary Comments on the Rationalization of Procedures for Processing Data Obtained from Nuclear Magnetic Resonance Studies

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Summary The procedures which should be used for correctly processing data obtained from n.m.r. studies of molecular complexes are stated, together with the conditions necessary for their use, and the results of the applications of these to studies of the reaction between chloroform and benzene in the presence of various inert materials are given.

NUCLEAR MAGNETIC RESONANCE spectroscopy may be used to study molecular complexes[1] formed in reactions of the type (1)

$$\mathrm{A} + \mathrm{B} \rightleftarrows \mathrm{A}\cdots\mathrm{B} \tag{1}$$

occurring in the presence of an inert material, S. The equilibrium quotient (K) for the reaction and the shift (Δ_C) induced in one of the species, say A, on the formation of a single, or of several isomeric 1:1 complexes,[2] may be deduced by two methods. First, an extrapolation method due to Benesi and Hildebrand,[3] which depends on the use of the familiar equation (2)

$$\frac{1}{\Delta_\mathrm{obs}} = \frac{1}{K[\mathrm{B}]_0\Delta_\mathrm{C}} + \frac{1}{\Delta_\mathrm{C}} \tag{2}$$

where $\Delta_\mathrm{obs} = \delta_\mathrm{obs} - \delta_\mathrm{free}$ and $\Delta_\mathrm{C} = \delta_\mathrm{C} - \delta_\mathrm{free}$, and δ_obs, δ_C, and δ_free are the shifts of A, observed, in the fully complexed state, and unassociated states respectively. Secondly, a data-processing method such as that used by Creswell and Allred.[4]

TABLE

Values of equilibrium quotients and Δ_c *for the chloroform–benzene reaction, in the presence of various inert materials at* 306·6 K

	(1)		(2)		(3)		(4)
Inert materials	K_x	Δ_c	K_x	Δ_c	K_c[a]	Δ_c	$K_\mathrm{c}(3)/K_\mathrm{x}(2)$[b]
Cyclohexane	1·4	90	1·5	84	0·14	84	0·091
cis-Decalin	1·7	83	1·7	79	0·16	79	0·091
Bicyclohexyl	1·9	80	1·9	77	0·17	76	0·090
Tetradecane	1·7	83	1·7	82	0·18	77	0·107
Hexadecane	1·7	84	1·7	82	0·16	81	0·095

[a] $\times\ 10^3\ \mathrm{m^3\ mol^{-1}}$

[b] $\times\ 10^3\ \mathrm{m^3}$. These ratios ase based on values of $K_\mathrm{x}(2)$ and $K_\mathrm{c}(3)$ computed to three significant figures.

It has been a matter of concern,[5] whichever method is employed for data processing, that (i) when a particular set of data is processed the value of Δ_C obtained is found to depend on the concentration scale used in the processing, and (ii) when a particular reaction is studied in different supposedly inert solvents, different values of Δ_C and the various equilibrium quotients are obtained. Understandably, there is a widespread feeling that there is a major ambiguity in n.m r. studies of molecular complexes that potentially undermines the utility of this approach. We wish to dispel this belief.

Whilst some workers[5] have claimed that (ii) is not found only if the molar scale is used for data processing, we do not support this claim and now *state* the procedure and related conditions which must be used to process data to avoid both anomalies (i) and (ii); the details of our investigations will be published later.

We have deduced on an entirely theoretical basis that: (A) Meaningful values may be obtained for the equilibrium quotients defined in terms of either mole fractions or molarities. This is only possible when x_B tends towards unity, under which conditions both equilibrium quotients are independent of the concentration of B and activity coefficients of all sorts, these requirements being necessary for the valid use of either of the two methods mentioned above. (B) The Benesi–Hildebrand method must be used for data processing, the parameters $K_{(\mathrm{x\ or\ c})}$ and Δ_C being obtained from the tangent to the appropriate curve where x_S is zero. (C) For the mole fraction scale, equation (2) must be modified to account for the variation of the shift of "free" species (A and A $\cdots$ B) with the composition of the mixtures, and the normal equilibrium expression must be modified to account for the effect of S (its size) in the mixtures. The operative form of the Benesi–Hildebrand equation then becomes (3)

$$\frac{1}{\Delta_\mathrm{obs} - [n_\mathrm{B}G/(n_\mathrm{B} + n_\mathrm{S})]} = \frac{n_\mathrm{B} + (V_\mathrm{S}n_\mathrm{S}/V_\mathrm{B})}{n_\mathrm{B}K_\mathrm{X}\Delta_\mathrm{C}} + \frac{1}{\Delta_\mathrm{C}} \tag{3}$$

where V_B and V_S are the molar volumes of B and S, and $G = (\sigma_\mathrm{A}^\mathrm{B} - \sigma_\mathrm{B}^\mathrm{B}) - (\sigma_\mathrm{A}^\mathrm{S} - \sigma_\mathrm{B}^\mathrm{S})$, $\sigma_\mathrm{j}^\mathrm{i}$ representing the screening effect of i on j infinitely dilute in i. (D) On the molar scale equation (2) is only modified by the function G since the correction for the size of S is implicit in this scale. (E) Rational values for K_X and Δ_C may only be obtained from the tangent to a plot of $1/[\Delta_\mathrm{obs} - n_\mathrm{B}G/(n_\mathrm{B} + n_\mathrm{S})]$ against $(n_\mathrm{B} + V_\mathrm{S}n_\mathrm{S}/V_\mathrm{B})/n_\mathrm{B}$ when the latter parameter is unity, and corresponding values for K_C and Δ_C may be obtained from the tangent to a plot of $1/[\Delta_\mathrm{obs} - n_\mathrm{B}G/(n_\mathrm{B} + n_\mathrm{S})]$ against $1/c_\mathrm{B}$ when $x_\mathrm{S} = 0$. For the studies many samples with $n_\mathrm{B}/(n_\mathrm{B} + n_\mathrm{S})$ varying between 0·9 and 1·0 have to be studied.

We have checked these assertions by investigating, amongst others, the reaction between chloroform and benzene with several compounds S which we are satisfied are sufficiently inert (in the n.m.r. sense). The first set of values for K_X and Δ_c in the Table were deduced by using equation (3), and the second set by omitting the term $n_B G/(n_B + n_S)$ in this equation. It can be seen that for *this reaction* the effect of correcting for G is small and can be neglected, and so the second set can be directly compared with the third set correspondingly deduced on the molar scale. Because of the implicit re-definition of K_X in equation (3), the ratio of K_c/K_X should equal the molar volume of benzene which in this case is $0{\cdot}0903 \times 10^{-3}$ m^3. The final column of the Table shows that indeed this is so, and validifies the approach. The main consequence of the treatment of the data is that Δ_c can be seen to be a parameter characteristic, within experimental and processing error, of the complex (or isomeric complexes), being independent of the nature of the inert material and the concentration scale adopted for the evaluation. We conclude therefore that for the reaction between chloroform and benzene *in benzene*, $K_X = 1{\cdot}7 \pm 0{\cdot}2$ and $K_c = 0{\cdot}16 \pm 0{\cdot}02 \times 10^{-3}$ m^3 mol^{-1} and $\Delta_c = 80 \pm 4$ Hz (at 60·004 MHz).

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[1] See *e.g.*, L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, 1964, and R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, 1969.

[2] I. D. Kuntz, jun. and M. D. Johnston, jun., *J. Amer. Chem. Soc.*, 1967, **89**, 6008.

[3] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.

[4] C. J. Creswell and A. L. Allred, *J. Phys. Chem.*, 1962, **66**, 1469.

[5] I. D. Kuntz, jun., F. P. Gasparro, M. D. Johnston, jun., and R. P. Taylor, *J. Amer. Chem. Soc.*, 1968, **90**, 4778, and references therein.