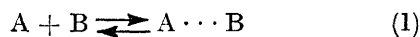


Molecular Complexes. Part XIII.¹ Confirmation for Methods proposed for rationalizing the Processing of Data obtained from Nuclear Magnetic Resonance Studies

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The interaction between chloroform and [²H₆]benzene in a variety of inert solvents has been investigated, and the chemical shift data processed using the mole fraction, molar, and molal concentration scales, rationalized, as described previously, to be consistent with the Benesi-Hildebrand method of analysis. It is shown that values obtained for Δ_c for any system are independent of the concentration scale used for its evaluation, and that the values obtained for K_x, K_c, and K_m are theoretically compatible.

RECENT investigations^{2,3} in this laboratory have been directed towards rationalizing methods of processing data obtained from n.m.r. studies of molecular complexes formed in reactions of the type (1) occurring in



the presence of a supposedly inert solvent, S.⁴ Fundamentally two types of procedures are generally used for processing data, namely, those based on the Benesi-Hildebrand⁵ and Creswell-Allred⁶ methods. These two procedures have been critically compared^{2,3} in the light of apparent anomalies concerning the results obtained therefrom. These anomalies were (a) that the chemical shift, Δ_c, induced in one species of the complex appeared to depend on the concentration scale used to process the data and (b) that K, the equilibrium quotient, and Δ_c appeared to depend on the supposedly inert solvents used for studying the reaction. It has been shown how these anomalies can be resolved.^{2,3} However, the earlier work depended on the measurement of chemical shifts with comparatively high error limits, being measured at 60 MHz on a non-field-frequency locked spectrometer. We now present confirmation for the procedures proposed previously using data of a higher accuracy than that available previously.

THEORY

Both the Benesi-Hildebrand and the Creswell-Allred methods of data processing depend on the Gutowsky-Saika⁷ theory of fast exchange in the form of equation (2)

$$\delta_{\text{obs}} = n_{\text{AB}}(\delta_{\text{c}} - \delta_{\text{free}})/n_{\text{A}} + \delta_{\text{free}} \quad (2)$$

where δ_{obs}, δ_c, and δ_{free} are the chemical shifts, from an arbitrary reference, of the solute (A) in a given sample, in the fully complexed situation, and in the uncomplexed, or free state, respectively, and n_{AB} and n_A are the equilibrium and initial numbers of moles of complex and solute respectively.

¹ Part XII, J. Homer and M. C. Cooke, *J.C.S. Faraday II*, in the press.

² J. Homer, M. H. Everdell, C. J. Jackson, and P. M. Whitney, *J.C.S. Faraday II*, 1972, **68**, 874.

³ J. Homer and P. M. Whitney, *J.C.S. Faraday I*, 1973, **69**, 1985.

⁴ See e.g. L. J. Andrews and R. M. Keefer, 'Molecular Complexes in Organic Chemistry,' Holden-Day, San Francisco, 1964; R. Foster, 'Organic Charge-Transfer Complexes,' Academic Press, New York, 1969 and references therein.

It has been suggested^{2,3} that the two anomalies quoted above can be avoided (a) by rationalizing the use of properties (concentrations on different scales) pertaining to samples in bulk with the molecular basis of equation (2), and (b) by using data processing procedures, e.g. the Benesi-Hildebrand method, under the correct thermodynamic conditions, this being necessary because it is known^{2,8} that the equilibrium quotient, K, is dependent on the range of concentration over which the interaction between solute (A) and aromatic substrate (B) is studied.

The n.m.r. analogue of the Benesi-Hildebrand method of data processing depends on equation (3), where Δ_{obs} =

$$\frac{1}{\Delta_{\text{obs}}} = \frac{1}{K[\text{B}]_0\Delta_{\text{c}}} + \frac{1}{\Delta_{\text{c}}} \quad (3)$$

δ_{obs} - δ_{free}, K and [B]₀ are respectively the equilibrium quotient (devoid of activity coefficients and thus wrongly considered to be independent of the composition of the reacting mixture) and the initial concentration of B appropriate to the scale used, and Δ_c is the chemical shift induced in A by B in the A ··· B complex.

There are three familiar concentration scales which can be used to describe [B]₀, namely, the mole fraction, molarity, and molality scales. Of these it has been suggested^{2,3} that the first and last must be modified to account for the molecular basis of equation (2). Additionally, the equilibrium quotients for each scale must be defined for conditions relating to the validity of the Benesi-Hildebrand equation (i.e. when [B]₀ ≫ [A]₀, and activity coefficients can be neglected), and should be given as in equations (4)–(6) respectively. From these definitions the relation-

$$K_{\text{x}} = \frac{n_{\text{AB}}(n_{\text{B}}V_{\text{B}} + n_{\text{S}}V_{\text{S}})}{(n_{\text{A}} - n_{\text{AB}})n_{\text{B}}V_{\text{B}}} \quad (4)$$

$$K_{\text{c}} = \frac{n_{\text{AB}}(n_{\text{B}}V_{\text{B}} + n_{\text{S}}V_{\text{S}})}{(n_{\text{A}} - n_{\text{AB}})n_{\text{B}}} \quad (5)$$

$$K_{\text{m}} = \frac{n_{\text{AB}}\rho_{\text{B}}(n_{\text{B}}V_{\text{B}} + n_{\text{S}}V_{\text{S}})}{(n_{\text{A}} - n_{\text{AB}})n_{\text{B}}} \quad (6)$$

ships, given in equation (7), between equilibrium quotients

$$K_{\text{x}}V_{\text{B}} = K_{\text{c}} = K_{\text{m}}/\rho_{\text{B}} \quad (7)$$

on the three concentration scales chosen may be deduced.

⁵ H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1948, **71**, 2703.

⁶ C. J. Creswell and A. L. Allred, *J. Phys. Chem.*, 1962, **66**, 1469.

⁷ H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, 1953, **21**, 1688.

⁸ J. Homer and M. C. Cooke, *J.C.S. Faraday I*, 1973, **69**, 1990.

The evaluation of each of the equilibrium quotients by the well proven Benesi-Hildebrand method, or the equivalent alternatives, has indicated^{2,3} the validity of the above

TABLE 1

The compositions of the mixtures employed in the investigation of the chloroform (A) + [²H₆]benzene (B) reaction in the presence of various inert materials (S), together with the corresponding chemical shifts of chloroform, measured relative to the shift^a of chloroform in the absence of [²H₆]benzene

10 ⁴ n _A /mol	10 ² n _B /mol	10 ³ n _S /mol	Δ _{obs} /Hz
S = Cyclohexane			
0.4858	3.2945	3.2425	83.10
0.4414	3.3195	2.8686	83.34
0.5553	3.3165	2.6015	83.59
0.4481	3.3531	2.1268	83.97
0.3727	3.3891	1.7925	84.54
0.3803	3.4180	1.4150	84.60
0.4615	3.4523	1.1370	85.17
0.3945	3.4985	0.7354	85.44
0.4087	3.5367	0.3701	85.81
S = <i>cis</i> -Decalin			
0.3333	3.2076	3.6506	92.12
0.3761	3.2423	3.2671	92.94
0.3493	3.3090	2.9290	93.38
0.3886	3.3412	2.5712	93.91
0.2982	3.3507	2.1835	94.48
0.3250	3.3869	1.8598	94.78
0.4372	3.4205	1.5156	95.09
0.3518	3.4955	0.8102	96.36
0.3534	3.5262	0.3634	97.08
S = Bicyclohexyl			
0.3543	3.2072	3.6502	84.84
0.6491	3.2444	3.2558	85.73
0.4665	3.2784	2.8863	86.33
0.3970	3.2805	2.5540	86.82
0.4959	3.3503	2.1774	87.28
0.3853	3.5213	1.8082	87.59
0.3426	3.4224	1.4325	88.16
0.3283	3.4582	1.0815	88.96
0.3476	3.4922	0.8044	89.22
0.3602	3.5287	0.3645	89.47
S = Tetradecane			
0.2948	3.2050	3.5517	85.90
0.5687	3.3083	3.1779	87.00
0.4833	3.2832	2.8180	87.80
0.4665	3.3161	2.4518	88.72
0.4339	3.4262	2.1371	89.16
0.3409	3.3907	1.7400	90.37
0.3124	3.4277	1.3609	91.09
0.3702	3.4849	1.0491	92.57
0.4213	3.5021	0.7001	93.55
0.4079	3.5311	0.3517	94.35
S = Hexadecane			
0.5009	3.2116	3.5296	84.94
0.4146	3.2459	3.1721	85.92
0.3769	3.2777	2.8212	87.21
0.4875	3.3224	2.4703	88.18
0.4959	3.3520	2.1305	89.00
0.4515	3.4470	1.4085	91.39
0.4037	3.4583	1.0536	92.24
0.3258	3.4964	0.7013	93.42
0.3375	3.5290	0.3481	94.39

^a An external tetramethylsilane lock was employed in the measurement of each value of δ_{free}.

relationships. We now confirm these indications by studies on a different interaction, namely [²H₆]benzene + CHCl₃, closely related to that investigated before.²

EXPERIMENTAL

The interaction between chloroform (at low and constant mole fraction of 0.001) and [²H₆]benzene (99.7% isotopic purity) was studied in the solvents cyclohexane, *cis*-decalin, bicyclohexyl, tetradecane, and hexadecane, in each case over a range of aromatic concentration between 0.9 and 1.0 mole fraction. Chemical shift measurements between chloroform and a suitable absorption from the solvent S (δ_{obs}) were made at 100 MHz on a Varian HA100D spectrometer in the field sweep mode, for which a lock signal was provided by the 0.3% proton impurity in the [²H₆]benzene. The low concentration of benzene used for the lock signal was insufficient to provide a signal which could readily be monitored on the oscilloscope in the usual manner, and so the 2.5 kHz lock signal was monitored using an audio amplifier to distinguish this signal from background noise aurally.

RESULTS

The concentrations and shifts for each sample are shown in Table 1. The temperature of the samples was determined in the conventional way by measuring the shift between the methyl and hydroxy-protons of methanol.

TABLE 2

Densities of the various materials used, at the temperatures of the investigations

T/K	10 ⁻³ ρ _B /kg m ⁻³ ^a	Solvent, S	10 ⁻³ ρ _S /kg m ⁻³
309.8	0.9299	Cyclohexane	0.7634 ^b
309.3	0.9305	<i>cis</i> -Decalin	0.8846 ^b
309.8	0.9299	Bicyclohexyl	0.88 ^c
309.5	0.9302	Tetradecane	0.7514 ^b
310.8	0.9287	Hexadecane	0.7622 ^b

^a Calculated for 99.7% isotopic purity from the data given by J. A. Dixon and R. W. Schiessler, *J. Amer. Chem. Soc.*, 1954, **76**, 2197, for 100 and 99.3% isotopic purity at several temperatures. ^b Deduced from the data given by J. Timmermans, 'Physico-chemical Constants of Pure Organic Compounds,' Elsevier, Amsterdam, 1965, vol. 2. ^c As a value at 309.8 K is not available from the literature, that provided by the supplier, Phase Separations Ltd., for the mixture of isomers was used (880 kg m⁻³ at 298.3 K).

The data were processed on an ICL 1905E computer using the modified^{2,3} Benesi-Hildebrand method of evaluation. The densities used in the computations are shown in Table 2, for each component studied. It should be pointed out that serious errors can arise from using the Benesi-Hildebrand method in conditions where several complexes of different stoichiometry coexist in solution. However, in the present work such errors are unlikely because chloroform can only complex with one benzene molecule in the energetically favoured orientation, and the concentration ratios are such that the binding of two chloroform molecules on opposite sides of a single benzene molecule is highly unlikely.

DISCUSSION

The values deduced for K_x, K_c, K_m, and Δ_c for each of the systems studied are shown in Table 3. The values obtained for Δ_c are the same for any particular solvent, irrespective of the concentration scale used for processing the data.

Table 3 also shows values for K_c/K_x and K_m/K_c which according to equation (7) should equal V_B and ρ_B respectively. Comparisons of the relevant values show remarkably good agreement, and provide strong support for the validity of using equations (4)–(6) for K_x , K_c , and K_m respectively.

Comparisons between the present work and that carried out previously^{2,3} show a significant (*ca.* 50%) increase in the values for equilibrium quotients determined here. There is also a significant decrease in the

footnote *c*) being used in the computation. However, it is more likely that the effect occurs because the bicyclohexyl molecule may be present with three forms of ring bonding, *viz.*, axial–axial, equatorial–equatorial, and axial–equatorial. In this case the polar forms, polarizability, and dielectric constant of the solvent could affect the number and nature of interactions present in solution so that the direct use of the Benesi–Hildebrand method would be invalidated and could lead to a spurious and high value for K .

TABLE 3

Values of parameters characteristic of the formation of the [²H₆]benzene + chloroform complex in various solvents

Solvent, S	K_x	$10^3 K_c/\text{m}^3$ mol ⁻¹	$K_m/\text{kg mol}^{-1}$	$\Delta_c(\text{p.p.m.})^a$	$10^3(K_c/K_x)/$ m ³ mol ⁻¹	$10^3 V_B/$ m ³ mol ⁻¹ (calc.)	$10^{-3}(K_m/K_c)/$ kg m ⁻³ (calc.)	$10^{-3} \rho_B/\text{kg}$ m ⁻³ (calc.)	T/K
Cyclohexane	2.1 ₈₃₈	0.19 ₈₂₇	0.18 ₄₅₇	1.2 ₅₄₁	0.09038	0.09048	0.9309	0.9299	309.8
<i>cis</i> -Decalin	2.4 ₇₃₉	0.22 ₃₇₁	0.20 ₈₁₄	1.3 ₆₈₈	0.09043	0.09042	0.9304	0.9305	309.3
Bicyclohexyl	2.9 ₇₂₆	0.26 ₈₆₆	0.25 ₀₁₀	1.2 ₀₅₆	0.09038	0.09048	0.9309	0.9299	309.8
Tetradecane	1.9 ₆₁₇	0.17 ₇₃₉	0.16 ₅₀₅	1.4 ₃₆₆	0.09043	0.09045	0.9304	0.9302	309.5
Hexadecane	1.9 ₁₃₄	0.17 ₃₆₈	0.16 ₁₃₃	1.4 ₆₄₃	0.09077	0.09059	0.9289	0.9287	310.8

^a The values obtained for Δ_c were identical for any particular solvent, whichever concentration scale was used for data processing.

values for Δ_c . Whilst it is possible that the replacement of hydrogen by deuterium in benzene could alter the parameters pertaining to the interaction with chloroform directly, it is more probable that differences in the interaction of benzene and [²H₆]benzene with the solvents used could result indirectly in an apparent change in the interaction parameters.

A further comparison between the benzene^{2,3} and [²H₆]benzene results shows that for both sets the values for the equilibrium quotients for the bicyclohexyl system are abnormally high, and differ significantly from the mean value for the other systems. This may be due to the presence of an undetected impurity or to an insufficiently accurate value for its density (Table 2,

It can be concluded that the present work substantiates the previous^{2,3} suggestions for rationalizing procedures for processing n.m.r. data obtained from studies of molecular complex formation. Moreover, it appears that these procedures facilitate the detection of meaningful differences between the values of K and Δ_c for quite similar reactions. However, it does appear that to provide reliable values for these two parameters at least two diluting solvents of the saturated hydrocarbon type employed here should be used.

We thank Professor W. G. S. Parker for facilities and the S.R.C. for a research studentship (to A. R. D.).

[3/1787 Received, 29th August, 1973]