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MOLECULAR COMPLEXES—IV[1]

EFFECT OF ADDITIONAL UNSPECIFIC SHIELDING (AUS). AUS CORRECTION OF NMR DATA APPLIED TO THE 1:1 COMPLEX FORMATION BETWEEN 1,3,5-TRIACETYL BENZENE AND BENZENE

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Abstract—Shifts of the two proton NMR signals of 1,3,5-triacetylbenzene (TAB) both relative to external and internal reference have been measured in CCl_4 solutions as function of the donor (C_6D_6) concentrations. A very large range of donor concentrations $[D_0]_i$ yielded plots of $\Delta_i/[D_o]_i$ vs Δ_i (simple Scatchard plots) which were distinctly curved. External referencing yielded upward curvatures, internal referencing even stronger downward curvatures.

The external referenced shifts were subjected to a linearizing procedure according to the modified Scatchard equation developed from the AUS concept. These independently from one another linearized Scatchard plots (for methyl and for aromatic signal) were exactly parallel, i.e. they gave exactly the same equilibrium quotient K. Performing the linearizing steps in the Cresswell-Allred procedure instead of the Scatchard procedure gave negligible deviations from the modified Scatchard K.

Determination of the equilibrium quotient K of a complex forming reaction between a donor D and an acceptor A by the NMR technique using varying excess concentrations of donor D is an often used method in spite of some methodical or general problems.[2–4] Some of these problems can be solved by using the proper concentration units, by using the best methods for treating the experimental data to evaluate K and the complex shift Δ_{AD}, and by seeing that complex parameters calculated from the experimental data by different modes will correspond with one another.[3] It has been argued (e.g. Ref.[3]) that the concentration units should be mol/l and it has been shown[3] that the Cresswell-Allred (–Gammon-Smallcombe–Richards) method and the Scatchard (–Foster–Fyfe) method will yield the most reliable complex parameters from the experimental data. Further, it has been shown[3] that the error introduced by the usual approximation of substituting the total donor concentrations $[D_o]$ for the concentrations of the free donor [D] can and should be eliminated by an iterative procedure.[5]

Observing these findings, there remains an experimental problem. That is the question, on which signal or which point should the acceptor signal be referred to in the different probes? Apart from the often discussed question "should the reference substance be applied externally or internally?", there is a second more subtle problem connected with this question. At least if the donor is aromatic and if K is not great one cannot expect a behaviour of the measured NMR shifts as it is demanded by the simple theory of 1:1 complex formation:[1] the signal of the equilibrated free acceptor does not hold its position but floats (highfield) on account of noncomplexing collisions with the (aromatic) donor molecules. That means, δ_A is not constant. This floating will be approximately a linear function of the donor concentration, i.e. it will be equal to $a_1[D_o]_i$. Likewise the not directly measurable position (δ_{AD}) of the complexed acceptor will float by approximately $a_2\ [D_o]_i$. The index i refers to the ith NMR probe.

From these floatings a modified Scatchard–Foster–Fyfe equation can be derived[1]:

$$\frac{\Delta_{oi}}{[D_o]_i} = -K(\Delta_{oi} - a_2[D_o]_i) + K\left(\Delta_{AD.oo} + \frac{a_1}{K}\right). \tag{1}$$

Discussing this equation it has been stated[1] that in the case of a curved Scatchard plot this modified equation (1) simply requires subtraction of a linear term $a_2[D_o]_i$ from the experimental Δ_{oi} in order to get a linear plot, and from this a better value for K.

Δ_{oi} is defined as the difference $\delta_{A.o} - \delta_i$. The index o in connection with a shift quantity refers to the condition $[D_o]_i = 0$.

The best value for the unknown AUS coefficient a_2 can be found by a trial procedure with a least squares sum as criterion. We term this procedure AUS correction.

Experimentally one should use an external reference signal. Since additive shift corrections on account of susceptibility variations have a linear dependence (provided the solution behaviour of D is ideal) on $[D_o]_i$ like the additive AUS correction one may include these susceptibility corrections in the AUS correction. Only the value of a_2 will be falsified thereby. As far as some arguments might favour an internal reference, these arguments will be matched by the AUS corrections. Besides, we[6] have found that an internal reference signal is influenced by an aromatic donor usually in a slightly nonlinear manner.

We are currently testing the AUS concept and the performance of the AUS corrections with different donor-acceptor systems,[6] one of which is the system 1,3,5-triacetylbenzene/benzene in carbon tetrachloride. We have selected this acceptor (TAB) because one statement of the AUS concept says that the coefficient a_2 will depend on the molecular position of the investigated acceptor nuclei.[1] The methyl protons and the aromatic protons of TAB should show a rather high difference in their respective a_2 values, the aromatic protons being far less accessible to collision influences than the Me protons. In order to be able to measure the aromatic shifts precis-

Table 1. Total C_6D_6 concentrations $[D_o]_i$ and measured shifts Δ_{oi}. The figures are taken from the computer output and are not rounded off. They are reproduced with more digits than may be considered meaningful

$[D_o]_i$ mol/l	H_{Ar}		Me	
	Δ_{oi} Hz	$\Delta_{oi}/[D_o]_i$ Hz·l/mol	Δ_{oi} Hz	$\Delta_{oi}/[D_o]_i$ Hz·l/mol
1.0778	9.866	9.1580	15.941	14.7963
1.6140	14.261	8.8400	23.296	14.4398
2.0797	17.923	8.6220	29.124	14.0098
3.1836	25.887	8.1347	42.278	13.2849
4.2490	33.060	7.7838	54.271	12.7773
5.3143	39.437	7.4238	65.227	12.2781
6.4289	46.151	7.1813	76.274	11.8683
7.4199	51.675	6.9669	85.674	11.5504
8.5346	57.413	6.7294	95.530	11.1969
9.6051	62.723	6.5324	104.747	10.9087
10.6625	67.819	6.3625	113.567	10.6543

ely the donor benzene had to be used in its deuteriated form.

Table 1 and Fig. 1 show the shifts Δ_{oi} and the simple Scatchard plots for both types of TAB protons. Note the upwards curvature of both plots which is to expect with an external reference.[1] When we referred to internal TMS the corresponding Scatchard plots were curved downwards the plot for the aromatic protons even showing a maximum in Δ_{oi}. We have evaluated K and complex shifts Δ_{AD} from the simple Scatchard plots of Fig. 1 (data of Table 1) and we have verified the results with our Cresswell–Allred[3] program. The four sets of complex parameters do not correspond very well and the complex shifts Δ_{AD} are rather large (Table 3).

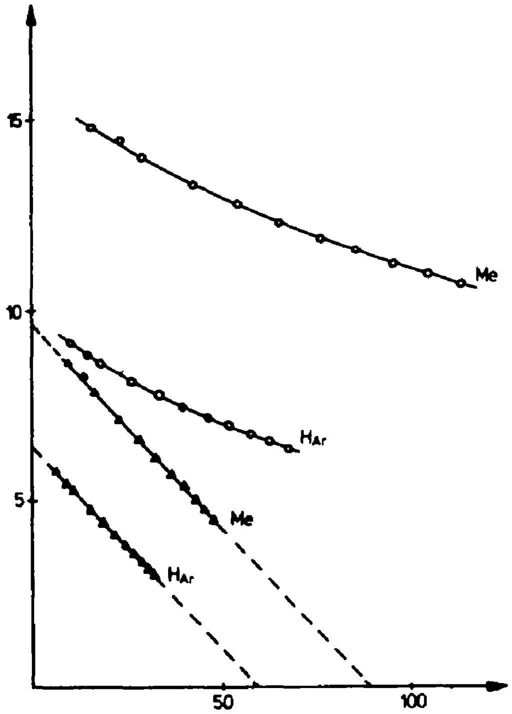

Fig. 1. ^{1}H-NMR Scatchard plots of TAB/benzene-d_6 in carbon tetrachloride. TAB signals, external reference. Upper plots —— O—O—O—O: According to the simple Scatchard equation (Foster–Fyfe equation): Abscissa: Δ_{oi}; Ordinate: $\Delta_{oi}/[D]_i$. Lower Plots Δ—Δ—Δ—Δ: After performing the AUS corrections according to the modified Scatchard eqn (2); Abscissa: $\Delta_{oi} - a_2[D_o]_i$; Ordinate: $\frac{\Delta_{oi} - a_2[D_o]_i}{[D]_i}$.

Before applying the AUS corrections we shall alter our modified Scatchard eqn (1) by a small transformation. Simply subtracting a_2 on both sides of the equation yields

$$\frac{\Delta_{oi} - a_2[D_o]_i}{[D_o]_i} = -K(\Delta_{oi} - a_2[D_o]_i) + K\left(\Delta_{AD\infty} + \frac{a_1 - a_2}{K}\right). \quad (2)$$

For convenience we define

$$\mathrm{Icpt} = K\left(\Delta_{AD,\infty} + \frac{a_1 - a_2}{K}\right).$$

This new form of the modified Scatchard equation (Scatchard modification 2)[6] avoids confusions which may arise from the simultaneous occurence of Δ_{oi} (left side) and the term $\Delta_{oi} - a_2[D_o]_i$ (right side) in eqn (1). In addition, eqn (2) makes the computer programs (Scatchard$_{IT}$ and Cresswell–Allred[3]) for performing the AUS correction simpler (the computations need less time) and the second term of the the right side (the intercept Icpt) will give a better approximation of $K\Delta_{AD,\infty}$ than the corresponding term of eqn (1). It must be pointed out that according to the AUS concept the complex shift cannot be determined precisely.[1]

The effect of the AUS correction on the Scatchard treatment according to eqn (2) can clearly be seen in Fig. 1. The plots have become linear *and* parallel. The small error which stems from substituting $[D_o]_i$ for $[D]_i$ in deriving eqns (1) and (2) has been eliminated by an iterative procedure[3] in the computer program (Sc$_{IT}$-AUS). The AUS corrected shift values are reproduced in Table 2.

To obtain the possibility of comparing complex para-

Table 2. AUS corrected shifts ($\Delta_{oi} - a_2[D_o]_i$). Comment as in Table 1

H_{Ar}		Me	
$\Delta_{oi} - a_2[D_o]_i$	$\frac{\Delta_{oi} - a_2[D_o]_i}{[D_o]_i}$	$\Delta_{oi} - a_2[D_o]_i$	$\frac{\Delta_{oi} - a_2[D_o]_i}{[D_o]_i}$
6.226	5.7819	9.277	8.6155
8.810	5.4636	13.316	8.2585
10.899	5.2454	16.265	7.8280
15.134	4.7576	22.593	7.1024
18.709	4.4064	27.999	6.5944
21.488	4.0462	32.367	6.0949
24.437	3.8036	36.523	5.6847
26.614	3.5891	39.795	5.3667
28.587	3.3515	42.759	5.0130
30.281	3.1543	45.357	4.7247
31.806	2.9845	47.639	4.4702

meters computed by different modes[3] of evaluation we have introduced the AUS correction into our Cresswell–Allred computer program[3] too.

Table 3 shows the very good correspondence between the four K values after performing the AUS correction. As it should be when only the 1 : 1 complex is involved the K value of this system is independent of the investigated acceptor nuclei (Me or aromatic) and independent of the mode of evaluation (Scatchard or Cresswell–Allred). In each of the four computations the final sum of least squares SDDQ ("sum of delta deviations quadratic") is much smaller than without AUS corrections (see Table 3). The four SDDQs are very similar to one another albeit the Cresswell-Allred evaluations again[3] turn out to be somewhat superior to the Scatchard evaluations. So we regard 0.104 l/mol as the best value for K.

The AUS correction leads not only to better corresponding K values but also to enlarged K values. So, Deranleaus demand regarding the range of saturation fraction[7] is met with better. This range extends from 0.10 to 0.53.

Both modes of evaluation (Sc_{IT}-AUS and CA-AUS) yield well corresponding values for a_2 and for Icpt/K, respectively. As had been expected, the AUS coefficient a_2 of the Me protons is appreciably greater than that of the aromatic protons. And, if we regard Icpt/K as an approximation for the complex shift, these values seem to us much more realistic than the large Δ_{AD} values without AUS correction. We do not yet understand why Me should have a larger complex shift than an aromatic proton. One explanation could be that complexed TAB is not planar but turns its O atoms away from the donor,

Table 3. Results of computations. Comment as in Table 1.
Without AUS corrections

Nuclei	H_{Ar}		Me	
Method	Sc_{IT}	CA	Sc_{IT}	CA
K l/mol	.0478±.0017	.0425	.0425±.0016	.0374
Δ_{AD} Hz	198.1±8.5	216.2±.9	359.0±16.3	395.9±1.6
SDDQ[a)]	1.9867	.8728	5.4599	2.3241

After AUS corrections

Method	Sc_{IT}-AUS	CA-AUS	Sc_{IT}-AUS	CA-AUS
K l/mol	.1078±.001	.1034	.1078±.001	.1041
Icpt/K Hz	59.6±.8	62.39±.19	89.2±1.1	92.74±.20
a_2 Hz·l/mol	3.3775	3.2969	6.1832	6.0811
SDDQ[a)]	.0777	.0731	.0928	.0852

[a)] SDDQ = sum of least squares (sum delta deviations quadratic) thus the Me groups bringing nearer to the donor. But this seems rather speculative as long as we do not know the magnitude of a_1. If, for instance, for both types of TAB protons $a_1 = 2a_2$, the real complex shifts $\Delta_{AD,\infty}$ would be 32 Hz for Me and 28 Hz for the aromatic protons. Besides, one cannot exclude that the difference $a_1 - a_2$ is rather small for the aromatic protons. Perhaps, the statement[1] that always $a_1 \geqslant a_2$ has been erroneous. If it is assumed that all (or most) of the (nearly) plane-parallel face-to-face collisions of free acceptor A with a donor molecule D will be complex forming then for the same type of collisions of the complexed acceptor the AUS influence may be greater, i.e. at least for this type of collisions the corresponding contribution to a_2 would be greater than its contribution to a_1.

EXPERIMENTAL

TAB Chemische Werke Hüls was twice recrystallized from ethanol, m.p. 163.5°. C_6D_6 Merck, Sharpe and Dome, degree of deuteriation $\geqslant 99\%$. Carbon tetrachloride p. a. Merck. NMR: HX-90 E Bruker, FT-spectra, 50 scans. NMR tubes Wilmad 527-pp together with precision coaxial spaced capillaries Wilmad 520-2. Reference external: 0.0138 mol/l $Me_3SiCD_2CD_2CO_2Na$ in D_2O (99.7%, Merck). Reference internal: 0.0061 mol/l. TMS. TAB concentration: $[A_o] = 0.01027$ mol/l.

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[6] The investigation of the floating of internal reference lines as well as the formulation of the Scatchard modification 2 was a piece of cooperation with J. Stafe who made the first successful application of the AUS concept (caffeine/benzene, to be published).

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