SOLVENT EFFECTS ON NMR SPECTRA OF GASES AND LIQUIDS†

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ABSTRACT

Solvent effects in gases have been treated on the basis of a binary collision model, which is then extended to liquids. The results indicate that the solvent effect can be approximated by a product of solute and solvent functions for systems involving nonpolar and polar solutes with isotropic nonpolar solvents. The anisotropy contributions from polar or nonpolar solvents can also be incorporated into the product function scheme.

INTRODUCTION

Solvent effects have been classified[1] as arising from bulk diamagnetic susceptibility, van der Waals forces, solvent anisotropy, electric field and electric field square terms, viz.

$$\sigma^{s}{}_{\mathrm{obs}} - \sigma_{\mathrm{gas}} - \frac{2}{3}\pi\chi_M = \sigma_w + \sigma_a + \sigma_E + \sigma_{E^2} \tag{1}$$

The quantity on the left hand side is the second virial shielding constant referred to the gas and corrected for the fact that cylindrical reference tubes have been used.

A theory for σ_w, σ_a, σ_E, σ_{E^2} has been given for the gas phase[2] and suitable refinements[3] and extension for liquids[4] have been attempted. This theory assumes only binary collisions so that the experiments are done in the linear pressure dependence range. In terms of other molecular properties[2]

$$\sigma_w = \frac{-\pi B N \alpha_2 I_2}{r_0^3}\left\{\frac{H_6(y)}{y^4} + \dots\right\} \tag{2}$$

where B is a property of the bonded magnetic nucleus under observation, α_2, I_2 are the polarizability and ionization potential of the solvent, $y = 2(\varepsilon/kT)^{\frac{1}{2}}$ where ε and r_0 are the constants of a Lennard-Jones potential and $H_n(y)$ functions have been tabulated by Buckingham and Pople[5].

It has been shown[2] that σ_E, σ_{E^2} may be expressed as

$$\sigma_E = -\frac{\pi N A}{6y^2}\left\{\frac{\mu_2\tau}{3}\cdot H_6(y) + \dots + \frac{4\alpha_2\mu_1}{r_0^3 y^2}\cdot H_6(y) + \dots\right\} \tag{3}$$

$$\sigma_{E^2} = -\frac{\pi N B}{3y^4}\left\{\frac{2\mu_2^2}{r_0^3}\,\mathrm{H}_6(y) + \dots\right\} \tag{4}$$

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where

$$\tau = \frac{\mu_1 \mu_2}{\varepsilon r_0^3}$$

with μ_1 and μ_2 being the electric moments of solute and solvent molecules respectively. A is a property of the bonded magnetic nucleus under investigation. Both A and B arise from assuming that the modified screening constant due to pair interaction is $-AE_z - B(E^2 + F^2)$ where E_z is the field along the bond, E^2 is the electric field squared, F^2 is the dispersion field squared.

Now it has been found that the neighbour anisotropy for gases is[2]

$$\sigma_a = \frac{-N\pi}{1080}(\chi_{\parallel} - \chi_{\perp})\{\tau^2 H_9(y) + \ldots\} \tag{5}$$

where $\chi_{\parallel} - \chi_{\perp}$ is the anisotropy of the diamagnetic susceptibility. It may be readily verified that this term is negligible for gases.

For liquids it becomes[6]

$$\sigma_a = -\tfrac{1}{3}(\chi_{\parallel} - \chi_{\perp})\frac{(3\cos^2\theta - 1)}{r^3} \tag{6}$$

If quadrupolar effects are included[2],

$$\frac{-\pi N A}{6y^2}\,\frac{2\mu_1 \theta_2^2}{y^2 k T r_0^5}\{H_8(y) + \ldots\}$$

should be added to equation 3 for the σ_E term where θ_2 is the quadrupole moment of the solvent.

Special cases of interaction arise for (a) nonpolar solute + isotropic solvent (b) nonpolar solute + anisotropic nonpolar solvent (c) nonpolar solute + anisotropic polar solvent (d) polar solute + isotropic solvent (e) polar solute + anisotropic nonpolar solvent (f) polar solute + anisotropic polar solvent (g) polar solute + proton acceptor, hydrogen bonding.

Thus the total second virial screening constant can be written for gases as

$$\sum = \sigma_{\text{obs}} - \sigma_{\text{gas}} - \frac{2\pi}{3}\chi_m = \sigma_w \left\{ 1 + \frac{2}{3}\frac{A}{B}\frac{\mu_1}{I_2} + \frac{A}{B}\frac{\mu_1 \mu_2^2 y^2}{18\varepsilon\alpha_2 I_2} + \frac{2\mu_2^2}{3\alpha_2 I_2} + \text{quadrupolar terms} + \text{terms in } H_{(n)} \text{ for } n > 6 \right\} \tag{7}$$

In the condensed phase and solutions etc., σ_a of equation 6 should be added to equation 7.

For case (a) $\mu_1 = 0, \quad \mu_2 = 0, \quad \Delta\chi = 0$

so $\sum = \sigma_w$ of equation 2

case (b) $\mu_1 = 0, \quad \mu_2 = 0, \quad \Delta\chi \neq 0$

For gases $\sum = \sigma_w$

For liquids $\sum = \sigma_w + \sigma_a$ (equation 6)

case (c) $\mu_1 = 0, \quad \mu_2 \neq 0, \quad \Delta\chi \neq 0$

For gases $\sum = \sigma_w + \sigma_{E^2} = \sigma_w\left\{1 + \dfrac{2\mu_2^2}{3\alpha_2 I_2}\right\}$ (8)

For liquids $\sum = \sigma_w + \sigma_{E^2} + \sigma_a$

case (d) $\mu_1 \neq 0, \quad \mu_2 = 0, \quad \Delta\chi = 0$

For gases and liquids

$$\sum = \sigma_w + \sigma_E = \sigma_w\left[1 + \frac{2}{3}\cdot\frac{A}{B}\cdot\frac{\mu_1}{I_2}\right] \tag{9}$$

case (e) $\mu_1 \neq 0, \quad \mu_2 = 0, \quad \Delta\chi \neq 0$

For gases $\sum = \sigma_w + \sigma_E$ as in equation 9

For liquids $\sum = \sigma_w + \sigma_E + \sigma_a$

$$= \text{equation } 9 - \frac{\Delta\chi}{3}\frac{(3\cos^2\theta - 1)}{r^3} \tag{10}$$

case (f) $\mu_1 \neq 0, \quad \mu_2 \neq 0, \quad \Delta\chi \neq 0$

For gases $\sum =$ as in equation 7

For liquids $\sum =$ equation 7 + σ_a (11)

case (g) $\mu_1 \neq 0, \quad \mu_2 \neq 0, \quad \Delta\chi \neq 0$, hydrogen bonding

$\sum$ for gases = equation 7 + H-bond

$\sum$ for liquids = equation 7 + H-bond + σ_a

where H-bond represents the contribution from hydrogen bonding.

Some general remarks may be made concerning the evaluation of the various contributions. It is apparent for example, that study of molecules of case (a) leads to evaluation of B for various types of bonded magnetic nuclei e.g. C—H (sp^3, sp^2, and sp types). An expression similar to equation 2 using only a scale factor turns out to be valid for liquids[4]. In this work we shall test whether equation 9 is applicable to liquids, case (d) and whether σ_a is independent of solute.

INTERACTION OF POLAR SOLUTE AND ISOTROPIC SOLVENT

It is clear that two kinds of experiments can be carried out. Gases may be studied by varying temperature and pressure, while solvent interactions may be studied in liquids and solutions.

In the discussion of the results obtained one may proceed in several ways. We tried to evaluate A and B for each type of bonded magnetic nucleus and then σ_a, the anisotropic term. The parameters found for gas mixtures were then carried over to liquids and solutions. In particular the equations found for the gases were used as a basis to obtain a rationale for solution and liquid results. This has been carried out for molecules of case (a) where it was shown that liquid and solution data for the van der Waals contribution could be obtained[4] from equation 2 after multiplication by an empirical factor. We shall assume here that with the same scale factor equation 9 is also valid for liquids and solutions.

Thus for example one can test the validity of the assumption that the medium effect depends only on the product of two functions, one characteristic of the solute only, and the other for the solvent. For σ_w we can assume the combining rules:

$$r_0 = (r_1 r_2)^{\frac{1}{2}}$$
$$y = (y_1 y_2)^{\frac{1}{2}}$$

which is equivalent to assuming

$$\varepsilon = (\varepsilon_1 \varepsilon_2)^{\frac{1}{2}}.$$

Assuming further that

$$H_6(y) = \{H_6(y_1).\, H_6(y_2)\}^{\frac{1}{2}}$$

then equation 2 for σ_w may be written

$$\sigma_w = -\left\{\frac{\pi N \alpha_2 I_2}{r_2^{\frac{3}{2}}}\left[\frac{H_6(y_2)}{y_2^{\frac{4}{2}}}\right]^{\frac{1}{2}}\right\}\cdot\left\{\frac{B}{r_1^{\frac{3}{2}}}\left[\frac{H_6(y_1)}{y_1^{\frac{4}{2}}}\right]^{\frac{1}{2}}\right\} \tag{12}$$

$$= \text{(a function of solvent only)} \times \text{(a function of solute only)}$$

$$= {}^2\sigma_w \times {}^1\sigma_w \tag{12a}$$

The upper left hand index indicates a solute 1 or solvent 2 contribution. Now the second term in brackets in equation 9 is the contribution coming from the induced field due to the polar solute and as can be seen has solvent dependence due to the ionization potential of the solvent. All other quantities A, B, are solute properties. It turns out that for the variety of solvents available for these experiments $1/I_2$ is constant to within about 10 per cent. Now for CH bonds for example this second term amounts to about 0.20 so that the error introduced by assuming $1/I_2$ is constant is only about ± 0.02 in 1.20 which is constant within the experimental accuracy. Thus the medium shift for polar solutes in isotropic solvents is a constant times the van der Waals effect; hence

$$\sigma = \sigma_w + \sigma_E = {}^2\sigma_w \times {}^1\sigma_w \times {}^1\sigma_E \tag{13}$$

where ${}^1\sigma_E$ is a constant factor for the solute and is essentially independent of the solvent. Treatment of the interactions in systems of nonpolar isotropic solutes and solvents as the product of solute and solvent contributions was suggested by Bothner-By[7] and rationalized in a manner analogous to equations 12 and 12a by Bernstein[8].

This has recently been taken up again by Malinowski[9] and coworkers and used in a powerful fashion to evaluate the anisotropic contribution of solvents. Besides the assumption of product functions[9] it has been assumed that the anisotropic contribution is also a product function of an extreme kind, namely only dependent on the solvent. There have been calculations based on this latter assumption which are not too unrealistic[10].

Our treatment of these data will proceed in a somewhat different manner. We shall indeed use the product function assumption. Instead of assuming σ_a is constant for a solvent, however, we assume that the equation for interaction in gases for polar solutes in isotropic and anisotropic solvents can be carried over to liquids and solutions. Since, in equation 9, μ_1/I_2 is small, and the second term is small for CH bonds, the observed data should be proportional to σ_w. One can then from experiments with polar solutes and anisotropic nonpolar solvents evaluate first the σ_E contribution and then the σ_a contributions and examine the assumption as to whether σ_a is only dependent on solvent. The results for gases are discussed first.

Gases

The experimental techniques were of two kinds. In the earlier experiments[2] gas samples were weighed in the sample tube under pressure to obtain the density. Since a very small amount of gas was weighed compared to the weight of the sample tube, large errors were encountered. In a more accurate set of experiments[11] the pressure was varied by introducing gas samples transferred at a known low pressure (*ca.* 3 atm) into the sample tube until the desired pressure was attained, so that a sample at 30 atm was obtained by 10 transfers of gas at 3 atm. Further, since ^{1}H shifts are small compared to the bulk susceptibility effect the latter experiments were carried out for ^{19}F resonance where now the large effect is the change in chemical shift.

Table 1 contains a matrix of solute/solvent data for ^{1}H and ^{19}F in gaseous mixtures. The method of obtaining $\sum$ for the pure gas and its mixtures has been previously described[2,11].

By using the data for the nonpolar solutes in the nonpolar isotropic solvents one can test the validity of the product function representation since the medium chemical shifts for one solute in a variety of solvents should be proportional to those for a different solute in the same solvents. From the data in *Table 1* one finds that the solute numbers for solution ratios

Table 1. $\sum$ in ppm for ^{1}H and ^{19}F resonance in gases at 300 K. Low field shifts are positive

		CF_4	SiF_4	SF_6	Kr	Xe	CH_4	C_2H_6	HCl	ref.
^{1}H	CH_4	10.3	19.7	12	13	34	6.7		21.3	11
	HCF_3	9					10	7		12
	$H_2C_2F_2$	−3	9	12	10	16.5	1	10	23	15
	HCl			22	33	44	26	36		2, 13
^{19}F	CF_4	198	239	316	247	458	222			11
	SiF_4	257	355	402	347	621	320			11
	SF_6	239	284	358	291	489	284			11
	HCF_3		152	183			140	189		12a
	$H_2C\ CF_2$	222	261	346	331	541	279	349	276	15

are as shown in *Table 2*. It is convenient to leave the CF_4 solute number as 1.00 for ^{19}F resonances. The solvent numbers then are in parts per million. These ratios represent the data within about ±5 per cent.

Figure 1 shows the agreement between the observed ^{19}F resonance for nonpolar solutes and solvents in the gas phase and those calculated with the above solute and solvent numbers. The worst discrepancy is for SiF_4 in

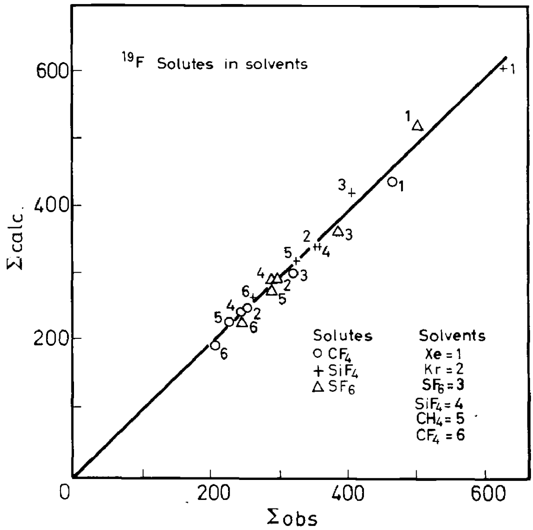


Figure 1. The observed medium shifts *vs.* those calculated from the product of the solute and solvent numbers of *Table 2.*

SF_6 i.e. $\frac{20}{400}$ or 5 per cent. This is better agreement than the values calculated from the collision theory with σ_{pair} attraction and repulsion terms[11], viz.

$$\sum = -\frac{\pi N B \alpha_2 I_2}{r_0^3}\frac{I_1}{I_1+I_2}\frac{H_6(y)}{y^4}\left[1 - c\frac{H_{16}(y)}{H_6(y)}\right]$$

Here the average error is about ± 15 per cent. We shall proceed therefore to evaluate the results on the basis of product functions (9 parameters) rather than the more fundamental collision theory (2 parameters).

Table 2. Solute and solvent numbers for second virial screening constant for gases.

	Relative solute number	Solvent number	
^{19}F	CF_4 = 1.00	CF_4	200
	SiF_4 = 1.39	SiF_4	248
	SF_6 = 1.19	SF_6	308
	HCF_3 = 0.62	Kr	254
	$H_2C{=}CF_2$ = 1.19	Xe	476
		CH_4	238
		HCl	~400
		C_2H_6	~310
^{1}H	CH_4 = 0.055		
	HCF_3 = 0.06		
	$H_2C{=}CF_2$ = 0.038		
	HCl = 0.13		

From equations 12a, 13 and 9 the ratio of two solute numbers, one polar S_I, and the other nonpolar S_{II}, is given by

$$\frac{S_I}{S_{II}} = \frac{\sigma_W^I \sigma_E^I}{\sigma_W^{II}}$$

$$= \frac{B_I}{B_{II}} \left[\frac{r_{II}}{r_I}\right]^{\frac{3}{2}} \left\{\frac{H(y_I)}{y_I^4} \cdot \frac{y_{II}^4}{H_6(y_{II})}\right\}^{\frac{1}{2}} \left\{1 + \frac{2}{3} \frac{A}{B} \frac{\mu_1}{I_2}\right\} \tag{14}$$

Where $1/I_2$ is the inverse of the ionization potential of solvent I is constant to about $\pm$10–15 per cent and is about 17. If B_I is assumed equal to B_{II} values of A/B can be calculated for some polar solutes from the molecular properties given in *Table* 3, and the solute ratios from *Table* 2.

Table 3. Molecular properties for the calculation of A/B

	ε/k	r_0	y	H_6/y_4†	μ	Solute number
$H_2C{=}CF_2$	272	4·50	1.91	7.0	1.4	1.19 for ^{19}F and 0·038 for ^1H
HCF_3	240	4.33	1.78	6.8	1.62	1.06 for ^{19}F and 0.06 for ^1H
$HCCl_3$	327	5.43	2.09	8·0	1.0	1.25 for ^1H
CF_4	152	4.70	1·43	6.0		1.00 for ^{19}F
CH_4	144	3.80	1.39	5.8		0.055 for ^1H
$C(CH_3)_4$	334	6.0	2.11	8.0		0.044 for ^1H
HCl	218	3.51	1.7	6.5	1.0	0.13 for ^1H

† A graph of this function against y has been given in reference 4.

These results are shown in *Table 4*.

Table 4. A/B values

Solute ratio	Resonance	Observed solute number ratio	$(A/B)_{CH}$	Calculated† $(A/B)_{CF}$	$(A/B)_{HCl}$	A/B Literature
HCF_3/CF_4	^{19}F	1.05		−2.0		−0.7 ± 0.4[a]
HCF_3/CH_4	^1H	1.095	3.7			3.7[b]
$H_2C{=}CF_2/CF_4$	^{19}F	1.19		~ 1.0		
$H_2C{=}CF_2/CH_4$	^1H	0.69	−3.8			
$HCCl_3/C(CH_3)_4$	^1H	1.25	2.0			
$HCl/C(CH_3)_4$	^1H	3.4			16.5‡	100 ± 35[c]

† for CH and CF the values are calculated from equation 14.
‡ for HCl the B_{HCl} value is assumed equal to that for $B_{C(CH_3)_4}$, which is a doubtful assumption.
[a] ref. 12.
[b] ref. 12 and ref. 11.
[c] ref. 2.

Note that since B is positive, A_{CH} in HCF_3 is positive while A_{CF} for the same molecule is negative. Also A_{CH} in $H_2C{=}CF_2$ is negative while A_{CF} in the same molecule is positive. The lack of agreement between the calculated and observed value of (A/B) for HCl could arise from the fact that B_{HCl} was assumed equal to B_{CH} in a methyl group and this is most certainly not so. In fact the data indicate that B_{HCl} is smaller than B_{CH}.

Liquids and solutions

It is possible to relate some of the gas results to those obtained in liquids. In gases the theory is for second virial screening constants where chemical shifts are obtained by dividing the second virial screening constant by a volume[2]. In liquids the theory is for chemical shifts.

For solutions equation 7 is written as

$$\Delta = \delta - \delta_{\text{gas}} - \frac{2\pi\chi_M}{3}$$

$$= \delta_w\left[1 + \frac{2}{3}\frac{A\mu_1}{B.\,I_2} + \ldots\right] + \delta_a \qquad (15)$$

where δ_a is the anisotropy contribution from equation 6 and δ_w is the van der Waals contribution in the liquid phase. For nonpolar solute and nonpolar isotropic solvents in the liquid phase it was found[4] that the liquid shift was proportional to the value calculated for the gas using the liquid density to give chemical shifts.

$$\text{Thus } \Delta \simeq \frac{K\Sigma}{V} = K\frac{{}^1\sigma_w\,{}^2\sigma_w}{V_2} \qquad (15a)$$

$$= (\text{Solute number}) \times (\text{solvent number}) \qquad (15b)$$

$$= {}^1\delta_w\,{}^2\delta_w \text{ say} \qquad (15c)$$

It is clear that the ratio of solute numbers for gases and liquids is the same†. For polar solutes in isotropic nonpolar solvents corresponding to equation 13 the medium shift is given by

$$\Delta_1^2 = {}^1\delta_w \cdot {}^2\delta_w \cdot {}^1\delta_E \qquad (16)$$

Again the ratio of solute numbers for the gases and liquids is the same. When the solvents are magnetically anisotropic we assume the solvent anisotropy effect to be independent of solute so that

$$\Delta_1^2 = {}^1\delta_w\,{}^2\delta_w\,{}^1\delta_E\,\delta_a \qquad (17)$$

For a series of polar solutes in a nonpolar anisotropic solvent then

$$\Delta_i^j = {}^i\delta_w\,{}^i\delta_E\,{}^j\delta_w + {}^j\delta_a$$

so that a plot of Δ_i^j *vs.* the solute numbers should be linear (if δ_a is a property of solvent only) with intercept δ_a and slope ${}^i\delta_E\,{}^i\delta_w$. The value for ${}^i\delta_E\,{}^i\delta_w$ is related to the gas value by equation 15a, i.e.

$${}^i\delta_E\,{}^i\delta_w\,{}^i\delta_w \equiv \frac{K \cdot {}^i\sigma_w\,{}^j\sigma_w\,{}^i\sigma_E}{v_j}$$

As *Figures 2–6*, and *9* show the plots of Δ_i *vs.* the gas values of the solvent number are indeed linear. Multiplying these gas solute numbers by a constant

† The relative solute ratios for solutions obtained by Raynes and Raza[16] are essentially the same as found here.

Table 5. ^1H resonance in solutions. $\sum$ in Hz, the + sign indicates a low field shift[a]

Solutes	$C(CH_3)_4$	$Si(CH_3)_4$	CCl_4	$SiCl_4$	C_6H_{12}	C_7H_{16}	CS_2	C_6H_6	$C_6H_5NO_2$	$CHCl_3$	$(CH_3)_2C{=}O$	CH_3CN
$C(CH_3)_4$	13.1	11.8	18.8	13.6	14.9		26.5	−12.5	−20.6	19.1	7.7	18.3
$Si(CH_3)_4$	14.2	11.4	19.7	14.8	13.9	13.2	29.5	−8.8	−16.4	19.5	8.2	19.9
C_6H_{12}	11.0	10.0	16.4	11.5	12.4	10.5	25.8	−16.0	−24.2	15.2	5.8	16.4
C_6H_6	15.9	13.7	24.2	16.7	12.5	12.3	29.4	−13.8	−5.6	28.7	18.6	26.4
$HCCl_3$	14.7		28.6	16.8	16.5	16.2	34.9	−65.2	11.1	30.1	64.0	48.9
$(CH_3)_2C{=}O$	15.9	14.9	29.0	19.5	16.4	15.6	34.7	−32.7	−3.8	34.1	18.6	28.2
CH_3CN	18.5	18.4	39.1	20.7	19.6	17.9	44.5	−79.1	6.8	41.1	31.7	37.1
HCl		40	71				85[b]	20		82[b]	17.9	283[b]
$(CH_3)_3{\equiv}C{-}\bar{H}$[b]		15.5	28.2				36.3	−1.7		39.3	49.7	50.4

[a] All data from W. T. Raynes unless otherwise indicated (unpublished).
[b] A. A. Grey, unpublished.

K will alter the slope of these lines but not the intercept, so the values of δ_a obtained in this way should be significant and determined by experimental error.

In *Table 5* a matrix of ^1H data is given which was measured by Raynes but not yet published[13]. These data allow one to obtain the solute and solvent numbers given in *Table 6*. Note that the solvent numbers obtained for the anisotropic liquids are a factor K times those for isotropic solvents and the values given in *Table 6* are for $K = 1$. For any other value of K, one need only divide the values in *Table 6* by this value to obtain the required solvent numbers. That K is not 1 can be seen from the fact that the two similar molecules C_6H_{12} and C_6H_6 have very different solvent van der Waals contributions, 273 and 608 respectively, corresponding to a K of $\frac{608}{273} \sim 2.2$.

Table 6. Solute and solvent numbers. (Hz at 60 Mcps) for liquid phase solutions

Relative solute number		Relative to $CF_4 = 1.00$	Solvent number in Hz		Solvent neighbour anisotropy, Hz
$C(CH_3)_4$	1.00	0.044	$C(CH_3)_4$	296	
$Si(CH_3)_4$	$\sim 1.08 \pm 0.04$	0.05	$Si(CH_3)_4$	251	
C_6H_{12}	0.83 ± 0.04	0.037	CCl_4	410	
nC_7H_{16}	0.73 ± 0.07	0.032	$SiCl_4$	296	
C_6H_6	1.20 ± 0.05	0.053	C_6H_{12}	273	
$HCCl_3$	1.25 ± 0.14	0.055	CS_2	571	3
$(CH_3)_2C{=}O$	1.27 ± 0.11	0.056	C_6H_6	608	−38
CH_3CN	1.6 ± 0.2	0.070	CH_3CN	341	3
HCl	3.4 ± 0.2	0.150	$CHCl_3$	421	0
$\equiv C{-}H$	1.39 ± 0.05	0.061	$(CH_3)_2C{=}O$	365	−8
$H_2C{=}CF_2$	0.86	0.038	$C_6H_5NO_2$	910	−60
CH_4	1.25	0.055			

As an example of how the numbers in *Table 6* can be used we may calculate the medium shift of $C(CH_3)_4$ in CCl_4 (in Hz) as $0.044 \times 410 = 18.0$ Hz. For C_6H_{12} in CS_2 for example one obtains $0.037 \times 541 + 3 = 23.6$ Hz (at 60 Mc).

The plot of $\Delta_i^{C_6H_6}$ *vs.* solute number is shown in *Figure 2*. The slope is 26.7 Hz, the intercept δ_a is -37.5 Hz. If K is around 1.5 as indicated in reference 4 the van der Waals contribution from C_6H_6 as a solvent is $\frac{2}{3} \times 26.7$, which is about 18 Hz. Thus for nonspecific interactions the neighbour anisotropy effect of benzene is nearly constant and equal to a high-field shift of 37.5 Hz at 60 MHz. It is clear from the points for $HCCl_3$ and CH_3CN in *Figure 2* that in the oriented pair there is an additional contribution to δ_a which is due to the specific interaction.

In *Figure 3* a corresponding plot is made for CS_2 as solvent. It seems that for CS_2, $\delta_w = 25.3$ Hz and $\delta_a = +3$. Note that for $HCCl_3$, acetone and CH_3CN, CS_2 behaves as if there was an average and constant amount of 3 Hz to take into account as neighbour anisotropy effect.

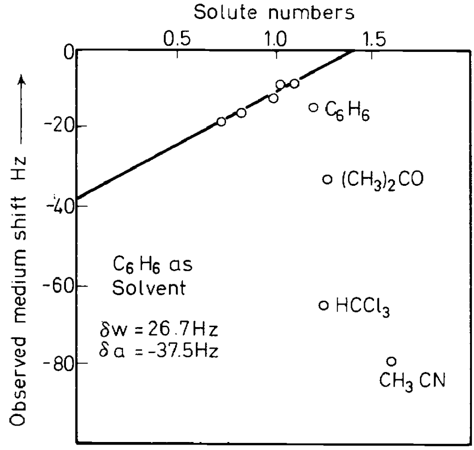


Figure 2. The medium shift of various solutes in benzene *vs.* the relative solute numbers of *Table 5.*

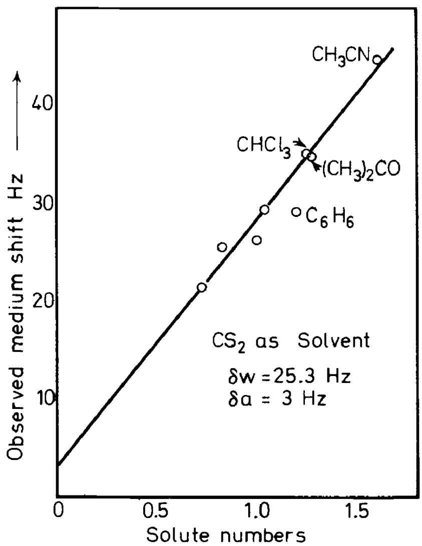


Figure 3. Observed medium shift of various solutes in CS_2 *vs.* the relative solute numbers of *Table 5.*

In *Figure 4*, one finds that $\delta_w = 15$ and $\delta_a = 3$ for CH_3CN as solvent. $CHCl_3$, acetone and CH_3CN are off the line because of specific interactions contributing to δ_a as well as dipole–dipole effects and hydrogen bonding. We expect $HCCl_3$ to give the largest low field shift due to electric field effects and this is observed.

In *Figure 5* we see that there is little or no neighbour anisotropy effect for $CHCl_3$ and that its solvent contribution is 18.5 Hz. Again the deviations from the straight line are due to special specific orientational effects such as hydrogen bonding.

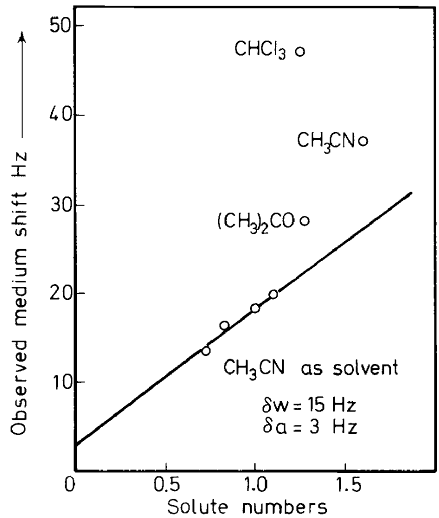


Figure 4. Observed medium shift of various solutes in CH_3CN *vs.* the relative solute numbers of *Table 5.*

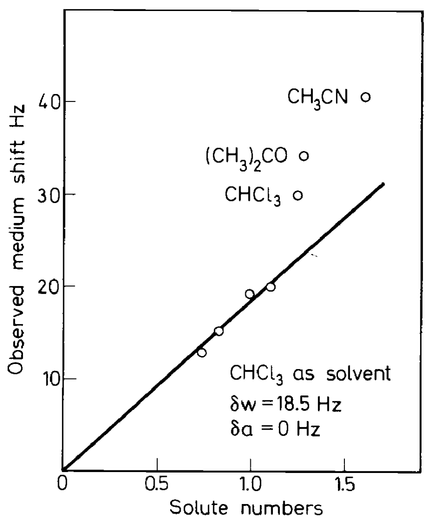


Figure 5. Observed medium shift of various solutes in $CHCl_3$ *vs.* the relative solute numbers of *Table 5.*

Figure 6 gives a linear plot for acetone as solvent and δ_w is 16.0 Hz while δ_a is -8 Hz. It is not surprising that $CHCl_3$ as solute in $(CH_3)_2C{=}O$ shows the greatest departure from the line due to hydrogen bonding and other specific orientation effects. These solvent numbers and the δ_as are also given in *Table 6*.

In *Figure 2* the observed medium shift for $HCCl_3$ in benzene is plotted against the solute ratios for CMe_4, $SiMe_4$, C_6H_{12}, and C_7H_{14}. It is clear that the intercept at solute number equal to zero gives δ_w while the slope gives δ_a for benzene in hertz. If the $HCCl_3$ ratio of 1.25 is used with this curve one finds that the shift due to anisotropy is about 97.5 and for CH_3CN

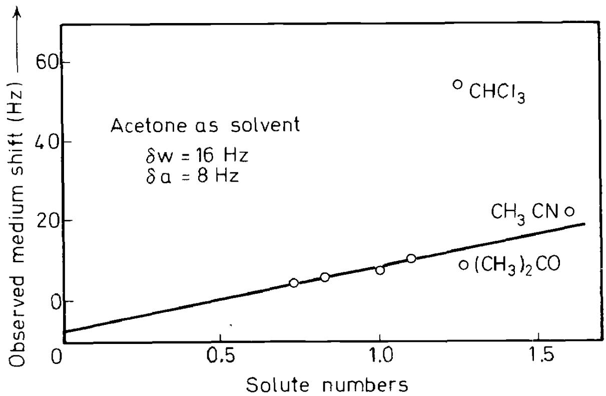


Figure 6. Observed medium shift of various solutes in acetone *vs*. the relative solute numbers of *Table 5*.

it is about 122 Hz. For the orientation where the C_{3v} axis of this molecule is collinear with the D_{6h} axis of benzene with the chloroform H atom nearest to the benzene ring we find for $HCCl_3$ using equation 6 that

$$\frac{97.5}{60} = 1.63 = \frac{\Delta\chi}{3}\frac{(3\cos^2\theta - 1)}{r^3} = \frac{10}{3} \times 9 \times \frac{2}{r^3} = \frac{60}{r^3}$$

so that $r = 3.92$ Å is found as the distance between the benzene ring and the H atom of chloroform. Now $r_0 = 5.43$ for $CHCl_3$ and 5.27 for C_6H_6; hence $r_{12} = 5.35$ Å. This is the distance expected for random orientation. Using this value of r in the above equation of the anisotropic contribution gives $60/5.35^3 = 23.5$ Hz. This may be compared with the value derived from *Figure 2* of 37.5 Hz.

If a plot similar to *Figure 2* is made for the various solute numbers and the shift observed in CS_2 as solvent (see *Figure 3*) it is clear, since both $HCCl_3$ and CH_3CN lie on the same curve as the other solvents, that CS_2 has no specific orientation with respect to the solutes of *Table 5* and acts only in a random fashion corresponding to an anisotropic contribution of $+3$ Hz.

From *Figures 2–5* one can obtain the van der Waals and neighbour anisotropy contributions for solutes and solvents and can then evaluate numerically the effect of electric field and hydrogen bonding on the various systems (see *Table 7*). These are polar molecules in polar solvents so that the contributions from dipole–dipole interaction, hydrogen bonding, and a value of δ_a consistent with the solute–solvent pair specific interaction, are expected. It is clear for example that $CHCl_3$ plus acetone gives a hydrogen

Table 7. Residual electric field and hydrogen bonding low field shifts in Hz.

Solute/Solvent	$CHCl_3$	Acetone	CH_3CN
CHCl	7	52	27
$(CH_3)_2C{=}O$	10	7	6
CH_3CN	11	14	10

bonded complex with a large low-field shift. The next strongest hydrogen bond is made with acetonitrile and this has a parallel in being the next largest medium shift.

Several values of the anisotropy of the diamagnetic susceptibility have been obtained from the Cotton Mouton effect[14]. Substitution in equation 6 gives the shielding due to the anisotropy of the solvent when the distance between the centre of the solute molecule and the centre of the solvent is known (see *Figure 7*).

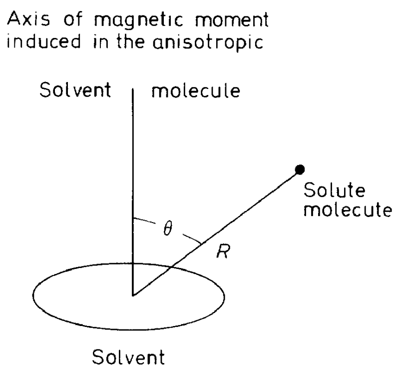


Figure 7. The neighbour anisotropy effect of an anisotropic solvent. For $\theta = 0°$ and $90°$ equation 6 gives $20\Delta\chi/3R^3$ (to high field) and $10\Delta\chi/3R^3$ (to low field) respectively.

In *Table 8* the $\Delta\chi$ obtained from Cotton Mouton constants are given and the contributions δ_a are calculated from the above equations in which r is taken as twice the close-packed radius calculated from the molar volume.

Table 8. δ_a, the neighbour anisotropy contribution to the chemical shift in Hz.

Solvent	$\Delta\chi$, cgs × 10^6†	δ_a Hz calc.	δ_a Hz obs.	r^3 calc.[a]	r^3 calc.[b]
$(CH_3)_2C{=}O$	7.08	−3	−8	178	60
$CHCl_3$	10.32	−2	~0	195	
CS_2	17.1	4	3	146	112
CH_3CN	3.6	1	3	127	380
C_6H_6	54.0	−17	−38	216	98

† Experimental values given in ref. 14.
[a] Calculated from equation 6 using $r = 2 \times$ radius of close-packed spheres obtained from molar volume.
[b] From equation 6 using obs. δ_a.

The calculated values with the selected r^3 values are meant to indicate only that the trend is similar to that for the observed values. One can use the observed values to obtain r and these values are shown in the last column of *Table 8*.

Neighbour anisotropy for specific interactions

From the data it is clear that $HCl + C_6H_6$ is very different from $HCCl_3 + C_6H_6$ and $\equiv C{-}H + C_6H_6$. Using the solute and solvent numbers for HCl, $(CH_3)_3C{-}C{\equiv}C{-}H$, and $HCCl_3$ as well as the solvent numbers for C_6H_6 and CS_2 we may calculate the neighbour anisotropy due to specific interaction with C_6H_6 and CS_2. The results are shown in *Table 9*. It is apparent that the neighbour anisotropy effect of benzene is not a constant for these solutions but depends on the specific geometry of the interacting pair. On the other hand, there seem to be no specific effects for CS_2 since the observed result can be calculated from the model.

Table 9. Neighbour anisotropy for specific interactions.

	δ† Calc.	δ obs.	δ_a specific
$\delta^{C_6H_6}_{HCl}$	91	20	−71
$\delta^{C_6H_6}_{\equiv C-H}$	37	−1.7	−39
$\delta^{C_6H_6}_{HCCl_3}$	34	−65·2	−99
$\delta^{CS_2}_{HCl}$	89	85	~0
$\delta^{CS_2}_{\equiv C-H}$	35.2	36.3	~0
$\delta^{CS_2}_{HCCl_3}$	32	35	~0

† From solute and solvent numbers of *Table 6*.

HCl as solute in various solvents requires some detailed considerations. From *Table 6* the ratio of the solute numbers

$$\frac{\delta^i_{HCl}}{\delta^i_{C(CH_3)_4}} = 3.4 \pm 0.2.$$

Table 10. Residuals in Hz (negative values are for high field shifts)

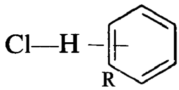
	$CHCl_3$	CH_3CN	acetone	CS_2	C_6H_6	C_6H_{12}
HCl (calc.)†	63	51	55	89	53	41
HCl (obs.)	82	283		85	20	50
polar–polar hydrogen bonding δ_a specific	19	232		~ −4	−35	~9

† From solute and solvent numbers of *Table 6*.

For HCl in various solvents we find the difference between the calculated and observed medium shifts for various solvents to give residuals made up of polar–polar effects, hydrogen bonding, and specific neighbour anisotropy effects (see *Table 10*).

From *Table 10* it is clear that for HCl in benzene, 53 is not the true anisotropic effect. From solute and solvent values for HCl and benzene a down field shift is calculated namely $3.4 \times 26.7 = 91$ Hz (see *Table 9*).

For the orientation in which the ClH axis is collinear with the six-fold symmetry axis of benzene,



the up field shift is (from equation 6)

$$\frac{20 \times 9}{3R^3} = \frac{60}{R^3} \text{ in parts per million.}$$

Equating this to the difference between the calculated and observed values, 91–20 = 71 Hz equals 1.2 ppm. We find $R^3 = 50$ and $R = 3{\cdot}7$ Å. The value for R is not unrealistic when one considers that the sum of the van der Waals radii of H and the benzene ring is $1.2 + 1.7 = 2.9$ Å whereas the sum of the radii of HCl and benzene derived from assuming close packed volumes is about 5 Å.

For HCl in CS_2 the shift due to neighbour anisotropy for HCl . . . . $\begin{matrix}S\\C\\S\end{matrix}$ is

$$\frac{10 \times 17.1}{3 \times 6} \times \frac{1}{R^3}$$

giving 5 Hz to low field if $R^3 \sim 125$. The calculated value for HCl in CS_2 is then $3.4 \times 25.3 + 5 = 91$ Hz. This value is not very different from the value observed (85 Hz).

The alkyl and alkyne proton medium shifts in $(CH_3)_3C—C{\equiv}C—H$

In *Table 11* are the corrected data for these medium shifts in various solvents. From a plot of the true data for $(CH_3)_3C—$ against the medium shift of $C(CH_3)_4$ (*Figure 8*) one obtains the gas phase value for $(CH_3)_3C—$ as 347.5.Hz. The gas phase value was not measured directly. Then from this value and the internal separation of the $(CH_3)_3C—$ signal from the $\equiv C—H$ signal in the same solvents the gas phase separation is 32.5 so that the gas value of 314.5 with the values for $\equiv C—H$ finally gives the $\equiv C—H$ medium shift in the last column of *Table 11*.

One may again calculate the medium shift for $\equiv C—H$ in a variety of active solvents and compare observed and calculated results (see *Table 12*). It is clear that for CS_2 and C_6H_6 there appear to be nonspecific neighbour anisotropy effects. For $CHCl_3$, CH_3CN and acetone there are specific effects due to solute–solvent pair geometry, e.g. specific neighbour anisotropy, polar–polar interactions and perhaps even hydrogen bonding.

It is interesting to compare C_6H_6 and nitrobenzene as solvents for polar molecules. In *Table 13* medium shifts for various solutes in $C(CH_3)_4$, C_6H_6 and nitrobenzene are given as well as those for the alkyne $\equiv C—H$ in

Table 11. True chemical shifts from benzene in Hz[b]

$C(CH_3)_4^a$	Solvents	$\delta(CH_3)_3C$	$\delta \equiv C—H$	χ_{corr}	Medium shifts $\Delta C(CH_3)_3$	$\Delta \equiv C—H$
18.8	CCl_4	325.0	286.3	9.9	22.5	28.2
26.5	CS_2	318.9	278.2	9.9	28.6	36.3
−12.5	C_6H_6	361.6	316.2		−14.1	−1.7
19.1	$CDCl_3$	324.0	275.2	14.8	23.5	39.3
18.3	CD_3CN	327.4	264.1	−14.3	20.1	50.4
7.7	acetone	337.1	264.8	−19.2	10.4	49.7
11.8	TMS	335.0	299.0	−8.9	12.5	15.5

[a] from *Table 5*.
[b] unpublished results of A. A. Grey, see *Table 5*.

pyridine. It is apparent from comparison of the $C_6H_6NO_2$ values with those where benzene is the solvent that for the nonpolar solutes the two solvents are giving high field shifts as expected (*Table 13*). Indeed the plot in *Figure 9* gives about 1.5 times the anisotropy effect of C_6H_6. For chloroform, while there is an upfield shift for the pair anisotropy with benzene, with nitrobenzene the interaction is with the nitro group and the H of chloroform giving a net low field shift.

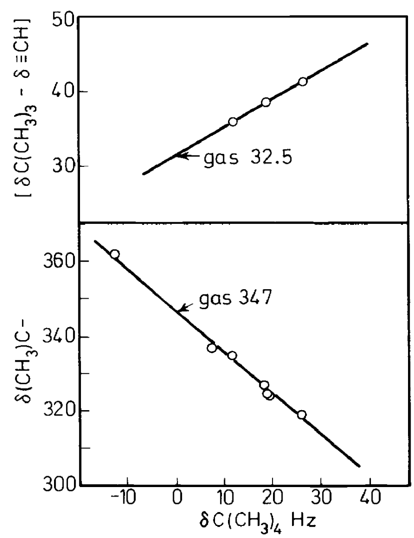


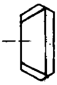
Figure 8. The internal chemical shift difference (upper) and the corrected chemical shift of the $(CH_3)_3C$ group in tertiary butyl acetylene *vs.* the medium shift of neopentane.

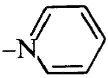
Table 12. Medium shifts for $\equiv C—H$.

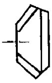
	$CHCl_3$	CH_3CN	CS_2	C_6H_6	$(CH_3)_2C{=}O$
$\equiv C—H$ calc.†	25.7	24	38	−11	14
$\equiv C—H$ obs.	39.3	50.4	36.3	−1.7	49.7

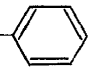
† From solute and solvent numbers of *Table 6*.

There is also a change in the geometry of the solute–solvent complex for acetone and CH_3CN as compared with benzene. For HCl in benzene and nitrobenzene the pronounced hydrogen bonding or dipole–dipole effect brings the resonance signal very far downfield. It is clear also that for ≡C—H in C_6H_6 the orientation is

$(CH_3)_3C—C≡C—H---$ 

In pyridine however we have $(CH_3)_3C—C≡C—H----$ 

For HCl in C_6H_6 we have ClH--- 

while in nitrobenzene we have Cl—H----O_2N— 

Finally it is interesting to compare the results (see *Table 4*) for HCl, $CHCl_3$ and ≡C—H in benzene. Using van der Waals radii it is readily shown that the Cl atoms are farther away from the benzene ring in $CHCl_3$

Table 13. Medium shifts in nitrobenzene in Hz.

	CMe_4	C_6H_6	$C_5H_5NO_2$	Solute numbers	Py
CMe_4	13.1	−12.5	−20.6	1.00	
$SiMe_4$	14.2	−8.0	−16.4	1.10	
C_6H_{12}	11.0	−16.0	−24.2	0.83	
nC_7H_{16}	11.3	−18.3	−31.7	0.70	
$HCCl_3$	14.7	−65.2	11.1		
$(CH_3)_2C{=}O$	15.9	−32.7	−3.8		
CH_3CN	18.5	−79.1	6.8		
HCl	43	20.0	223.5	3.4	
≡C—H	15.5	−1.7		1.4	48.4

than the Cl atom in HCl. Since the distance is larger the repulsion is less and chloroform can move its hydrogen closer to the benzene ring than HCl can accounting for the much greater high field shift. For $(CH_3)_3C—C≡C—H$ several benzene molecules can be accommodated around this molecule so the perpendicular configuration in which the plane of a benzene molecule is perpendicular to the ≡C—H axis is unlikely. It might be easier to put two benzene molecules at this end inclined at an angle to each other and the

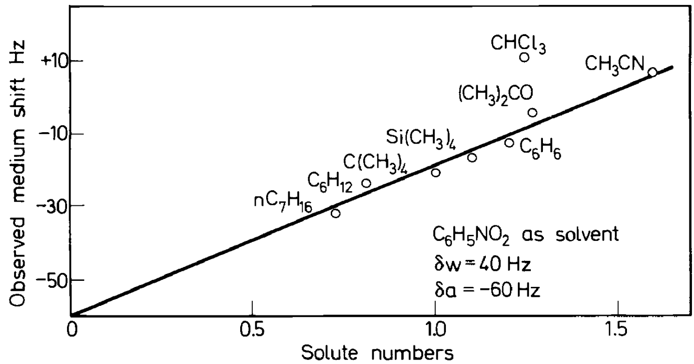


Figure 9. Observed medium shift of various solutes in nitrobenzene *vs.* the relative solute numbers of *Table 5*.

C≡C—H axis. This would reduce the neighbour anisotropy effect by the factor $(3\cos^2\theta - 1)$.

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