The Determination of Magnetic Susceptibilities by a New Nuclear Magnetic Resonance Method

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Summary A new n.m.r. technique for the determination of magnetic susceptibilities is described, and the results of its application to several organic compounds are given.

Following the work of Becconsall *et al.*,[1] a method of determining magnetic susceptibilities has been devised which uses the differences between externally referenced chemical shifts caused by the difference in sample configuration in two spectrometers, one having a conventional magnet which applies the field perpendicular to the sample axis (⊥) and the other a superconducting solenoid which applies the field longitudinally (‖).

For a cylindrical reference vessel coaxial with the main sample tube, the relative shift for a reference compound at infinite dilution in two solvents x and y in the two regions of the sample cell are, for the perpendicular and parallel field orientations, given,[1] respectively, by equations (1) and (2). In these equations $\chi_{v(i)}$ is the volume susceptibility

$$\overset{\perp}{\sigma}_{\mathrm{sol(y)}} - \overset{\perp}{\sigma}_{\mathrm{sol(x)}} = \frac{2\pi}{3}\left[\chi_{v(\mathrm{y})} - \chi_{v(\mathrm{x})}\right] + \sigma_{\mathrm{loc(y)}} - \sigma_{\mathrm{loc(x)}} \tag{1}$$

$$\overset{\parallel}{\sigma}_{\mathrm{sol(y)}} - \overset{\parallel}{\sigma}_{\mathrm{sol(x)}} = -\frac{4\pi}{3}\left[\chi_{v(\mathrm{y})} - \chi_{v(\mathrm{x})}\right] + \sigma_{\mathrm{loc(y)}} - \sigma_{\mathrm{loc(x)}} \tag{2}$$

of i and $\sigma_{\mathrm{loc(i)}}$ is the sum of all the screening effects of the solvent, except that of its susceptibility, on the solute. From equations (1) and (2) it follows that the difference between the shifts measured for the solute in the perpendicular ($\delta^{\perp}$) and parallel ($\delta^{\parallel}$) field orientations is given by equation (3).

$$\left[\overset{\perp}{\sigma}_{\mathrm{sol(y)}} - \overset{\perp}{\sigma}_{\mathrm{sol(y)}}\right] - \left[\overset{\parallel}{\sigma}_{\mathrm{sol(y)}} - \overset{\parallel}{\sigma}_{\mathrm{sol(x)}}\right] = (\delta^{\perp} - \delta^{\parallel}) = 2\pi[\chi_{v(\mathrm{y})} - \chi_{v(\mathrm{x})}] \tag{3}$$

The factor of 2π in equation (3) corresponds fundamentally to the shape factor for a transversely oriented cylindrical sample as originally invoked by Dickinson.[2] When implementing equation (3) for the determination of magnetic susceptibilities, a value for the shape factor for the chosen reference vessel may be deduced experimentally using a series of solvents x and y of known susceptibilities, as has been done by other workers when using equations similar to (3).[3] However, the value for the shape factor so deduced must depend on the collective uncertainty in classically obtained susceptibilities, and this may be considerable. It appears, therefore, that little is to be lost by assuming the validity of the theoretical value for the shape factor for a well-made reference vessel and using a single solvent whose susceptibility is well-documented, in order to obtain values for the susceptibilities of other materials. In this work, this latter approach has been adopted initially, using benzene as the reference solvent. The reference solute chosen was cyclohexane because this is believed to be inert (in the n.m.r. sense),[4] and the solutions studied contained this material at a mole fraction of *ca.* 0·005. Whilst infinitely dilute solutions should be used theoretically the effect of the presence of a finite amount of the solute should be negligible because the same concentration was used in both solvents in a particular experiment.

The chemical shifts were measured at 306 K using a Wilmad precision capillary coaxial with 5 mm O.D. tubes on a Varian 220 MHz instrument and a Perkin-Elmer R 10 spectrometer, operating at 60·004 MHz. The chemical shifts of cyclohexane in several solvents are given in Table 1, together with the values of the volume susceptibilities deduced therefrom. It can be seen that the experimental susceptibility values generally agree well within 1% of the literature values. Similar agreement can be seen in Table 2 which presents the shifts obtained by Becconsall *et al.*,[1] at the ambient temperature, and the corresponding susceptibility values.

It is interesting to note that if $\delta^{\perp}$ and $\delta^{\parallel}$ were measured at different temperatures equation (3) would no longer apply due to the temperature dependence of $\sigma_{\mathrm{loc(i)}}$. In order to estimate the significance of this temperature dependent effect we have investigated several systems at 293 and 306·6 K on the 220 and 60 MHz instruments, respectively. If $\sigma_{\mathrm{loc(i)}}$ is assumed to be independent of temperature, equation (3) may be rewritten conveniently in terms of specific susceptibilities as in equation (4).

$$\overset{\perp}{\delta}_{T_2} - \overset{\parallel}{\delta}_{T_1} = \frac{2\pi}{3}\left\{\chi_{(\mathrm{y})}\left[\overset{T_2}{\rho}_{(\mathrm{y})} + 2\overset{T_1}{\rho}_{(\mathrm{y})}\right] - \chi_{(\mathrm{x})}\left[\overset{T_2}{\rho}_{(\mathrm{x})} + 2\overset{T_1}{\rho}_{(\mathrm{x})}\right]\right\} \tag{4}$$

where $\chi_{(\mathrm{i})}$ is the specific susceptibility of i and $\rho_{(\mathrm{i})}^{T_j}$ is the density of i at temperature T_j. The shifts obtained at two temperatures for several systems are given in Table 3, together with the appropriate values of the specific susceptibilities deduced using equation (4). It can be seen that the approximate experimental values agree quite well with the literature values of the susceptibilities. It appears therefore that over the small temperature range used here, the effect of the temperature dependence of screening effects other than susceptibility is small and may, if necessary, be ignored when obtaining susceptibility data.

The method described here has some advantages over the two main established n.m.r. techniques[5,6] for determining magnetic susceptibilities. The method due to Frei and Bernstein[5] requires the simultaneous use of a spherical and a cylindrical reference vessel with the result that the relevant equation corresponding to (3) is governed by a shape factor whose theoretical value is one third of that given above. Consequently, any experimental departures from geometric ideality of the *two* vessels may lead to higher percentage inaccuracies than that pertaining to the single vessel situation considered here. The method of Reilly *et al.*,[6] although requiring no more than a precision coaxial cylindrical reference vessel, does necessitate careful adjustment of a conventional spectrometer to obtain optimum results. The technique described here requires neither special adjustments to the spectrometer nor such extensive calibration of the cell as is necessary for the method of Reilly *et al.*

It appears that this method may afford rapid and accurate determinations of magnetic susceptibilities. Undoubtedly the results in Tables 1 and 3 can be further improved by the more precise measurement of $\delta^{\perp}$ at higher spectrometer frequencies.

TABLE 1

Solvent induced shifts (p.p.m.) for cyclohexane, and solvent (y) volume magnetic susceptbilities at 306·6 K

Solvent x	Solvent y	$-\delta^{\perp}$	$-\delta^{\parallel}$	$-\chi_v(\text{exp}) \times 10^6$	$-\chi_v(\text{lit}) \times 10^6$[a]
Benzene[b]	Toluene	$0{\cdot}063_2$	$0{\cdot}035_2$	$0{\cdot}611_5$	0·6132
	p-Xylene	$0{\cdot}096_5$	$0{\cdot}046_5$	$0{\cdot}615_0$	0·6143
	m-Xylene	$0{\cdot}097_6$	$0{\cdot}032_8$	$0{\cdot}617_4$	0·6149
	o-Xylene	$0{\cdot}146_2$	$-0{\cdot}051_1$	$0{\cdot}638_5$	0·6356
	Chlorobenzene	$0{\cdot}245_2$	$-0{\cdot}190_0$	$0{\cdot}676_4$	0·6777
	1,2-Dichlorobenzene	$0{\cdot}463_2$	$-0{\cdot}330_0$	$0{\cdot}733_3$	0·7400
	Chloroform	$0{\cdot}772_3$	$0{\cdot}018_1$	$0{\cdot}727_2$	0·7277
	Carbon tetrachloride	$0{\cdot}699_7$	$0{\cdot}229_8$	$0{\cdot}681_9$	0·6788
	Carbon disulphide	$0{\cdot}824_1$	$0{\cdot}350_7$	$0{\cdot}682_5$	0·6896

[a] These data are not available unambiguously, and so for consistency the values quoted are those calculated from the specific susceptibilities given in ref. 7 and the densities at 306.6 K extrapolated from those given in ref. 8. [b] The value of χ_v for benzene has been taken to be $-0{\cdot}6071 \times 10^{-6}$.

TABLE 2

Solvent induced shifts (p.p.m.) for Me_4Si, and solvent (y) volume magnetic susceptibilities at ca. 288 K

Solvent x	Solvent y	$\delta^{\perp}$	$\delta^{\parallel}$	$-\chi_v(\text{exp}) \times 10^6$	$-\chi_v(\text{lit}) \times 10^6$[a]
Carbon tetrachloride	Benzene	0·67	0·21	$0{\cdot}62_{13}$	0·6207
	Pyridine	0·80	0·23	$0{\cdot}60_{38}$	0·6173
	Carbon disulphide	−0·16	−0·12	$0{\cdot}68_{81}$	0·6861
Cyclohexane	Benzene	0·40	0·44	$0{\cdot}64_{05}$	0·6207
	Pyridine	0·54	0·46	$0{\cdot}62_{13}$	0·6173
	Carbon disulphide	−0·41	0·11	$0{\cdot}71_{68}$	0·6861

[a] See footnote to Table 1; the relevant temperature is now 288 K.

TABLE 3

Solvent susceptibilities deduced from the induced shifts of cyclohexane at two temperatures

Solvent x	Solvent y	$-\delta^{\parallel}$[a]	$-\chi(\text{exp}) \times 10^6$	$-\chi(\text{lit}) \times 10^6$
Benzene	Toluene	$0{\cdot}035_5$	$0{\cdot}716_4$	0·7176
	p-Xylene	$0{\cdot}045_3$	$0{\cdot}725_5$	0·7232
	m-Xylene	$0{\cdot}038_8$	$0{\cdot}724_3$	0·7212
	o-Xylene	$-0{\cdot}033_5$	$0{\cdot}732_9$	0·7327
	Chlorobenzene	$-0{\cdot}184_8$	$0{\cdot}619_2$	0·6216
	1,2-Dichlorobenzene	$-0{\cdot}413_0$	$0{\cdot}579_0$	0·5734
	Chloroform	$0{\cdot}022_0$	$0{\cdot}495_1$	0·497
	Carbon tetrachloride	$0{\cdot}023_8$	$0{\cdot}434_1$	0·433

[a] At 293 K: $\delta^{\perp}$ as in Table 1.

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