

Bulk Susceptibility Corrections in Nuclear Magnetic Resonance Experiments Using Superconducting Solenoids

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WHEN A NUCLEAR magnetic resonance (NMR) spectrum is referenced with an external standard contained either in a capillary inserted coaxially in a cylindrical sample or in the annular region of a coaxial sample, the observed chemical shift must be corrected for the difference in the bulk susceptibilities of the sample and the reference compound (1). This problem has been treated at length for the conventional magnet/sample configuration, such as that of the Varian A-60 or HA-100 spectrometer, where the applied polarizing magnetic field is transverse to the long axis of the cylindrical sample (2). For this magnet/sample geometry, the bulk susceptibility correction to the observed chemical shift has been shown to be

$$\delta_{\text{corr}} = \delta_{\text{obs}} + \frac{2\pi}{3} (\chi_v^{\text{ref}} - \chi_v) \quad (1)$$

where δ_{obs} is the observed chemical shift, δ_{corr} is the chemical shift corrected for bulk susceptibility, and χ_v , χ_v^{ref} refer to the volume magnetic susceptibilities of the sample and reference solutions, respectively.

Recently, high-field NMR spectrometers, such as the Varian HR-220, have come into use, where superconducting solenoids are used to generate the magnetic field (3). When cylindrical samples are employed in these instruments, the polarizing magnetic field is along the long axis of the sample. The bulk susceptibility correction for chemical shifts referred to an external reference compound contained in a capillary or in the annular region of coaxial sample containers is then no longer given by Equation 1 because of different magnetic polarization of the sample. The effective magnetic field experienced by a molecule in the sample is given by

$$\vec{H}_{\text{eff}} = \vec{H}_0 + \vec{h}_1 + \vec{h}_2 \quad (2)$$

where \vec{H}_0 is the applied magnetic field, \vec{h}_1 is the familiar demagnetization field due to the induced magnetism on the external sample boundary, and \vec{h}_2 is the Lorentz field due to induced magnetism on the surface of the Lorentz sphere encompassing the molecule. Both \vec{h}_1 and \vec{h}_2 are proportional to the magnetization induced in the sample: $\vec{h}_1 = -\alpha\chi_v\vec{H}_0$, where α is the demagnetization factor and is dependent on the shape of the sample, and $\vec{h}_2 = \frac{4\pi}{3}\chi_v\vec{H}_0$. For the polarizing magnetic field parallel to the long axis of cylindrical samples, $\alpha = 0$. Hence

$$\vec{H}_{\text{eff}} = \vec{H}_0 \left(1 + \frac{4\pi}{3} \chi_v \right) \quad (3)$$

from which it is readily shown that

$$\delta_{\text{corr}} = \delta_{\text{obs}} - \frac{4\pi}{3} (\chi_v^{\text{ref}} - \chi_v) \quad (4)$$

A comparison of Equations 1 and 4 indicates that the bulk susceptibility correction in the case of the HR-220 magnet/

sample geometry is *twice* in magnitude (in ppm) and of the *opposite* sign from that expected in the case of conventional spectrometers.

We have verified this result experimentally by comparing the effects of DPPH (2,2-diphenyl-1-picrylhydrazyl) on the HA-100 and HR-220 spectra of TMS in CHCl_3 relative to the corresponding spectra of the undoped solution contained in a capillary. In these experiments, the resonance position of TMS in the free radical doped solution is shifted from its position in the undoped capillary, primarily due to the change in the bulk susceptibility of the solution resulting from the paramagnetism of the added DPPH. As shown in Figure 1a, the broadened TMS signal in the doped solution is shifted 0.196 ppm upfield in the HA-100 spectrum, whereas in the HR-220 spectrum of the same sample this TMS signal is located 0.394 ppm downfield from the capillary TMS signal. The observed ratio of the HR-220 to HA-100 bulk susceptibility shifts is -2.01 , which is in excellent agreement with the expected theoretical ratio.

Clearly, from the above considerations, the larger bulk susceptibility shifts on the HR-220 spectrometer, together with the additional dispersion of chemical shifts at the higher NMR frequency, make the HR-220 spectrometer particularly suitable for paramagnetic susceptibility determinations (4). The different effects of bulk susceptibility on HA-100 and HR-220 spectra also suggest a convenient and simple method for separating specific solvent perturbations on chemical shifts from bulk susceptibility effects. In Figure 1b, the HA-100 and HR-220 spectra of TMS in CHCl_3 are compared with the TMS signal of the neat liquid sealed in a capillary. Although the expected effect of bulk susceptibility differences between the bulk and capillary solutions is qualitatively reflected in the spectra, the observations are not in quantitative agreement with the predictions of Equations 1 and 4. The discrepancy lies, of course, in differences in the solvent interactions of TMS with itself and TMS with CHCl_3 . Equations 1 and 4 can be generalized to include the solvent shift as follows:

$$\delta_{\text{corr}} - \delta_s = \delta_{\text{obs}} + \frac{2\pi}{3} (\chi_v^{\text{ref}} - \chi_v) \quad (1')$$

$$\delta_{\text{corr}} - \delta_s = \delta_{\text{obs}} - \frac{4\pi}{3} (\chi_v^{\text{ref}} - \chi_v) \quad (4')$$

These equations can be solved simultaneously for the solvent shift, δ_s , and $\Delta\chi = \chi_v^{\text{ref}} - \chi_v$. For the system at hand, $\Delta\chi$ was found to be $+0.199$ ppm, which is in excellent agreement with the value of $+0.197$ ppm calculated from published magnetic susceptibility data (5). The difference in solvent perturbations on the chemical shift was found to be 0.128 ppm downfield in going from the neat TMS liquid to TMS dissolved in CHCl_3 .

(1) W. C. Dickinson, *Phys. Rev.*, **81**, 717 (1951).
(2) J. R. Zimmerman and M. R. Foster, *J. Phys. Chem.*, **61**, 282 (1957).
(3) J. K. Becconsall and M. C. McIvor, *Chem. Brit.*, **5**, 147 (1969).

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(5) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Ltd., London, 1965, pp 262, 608.

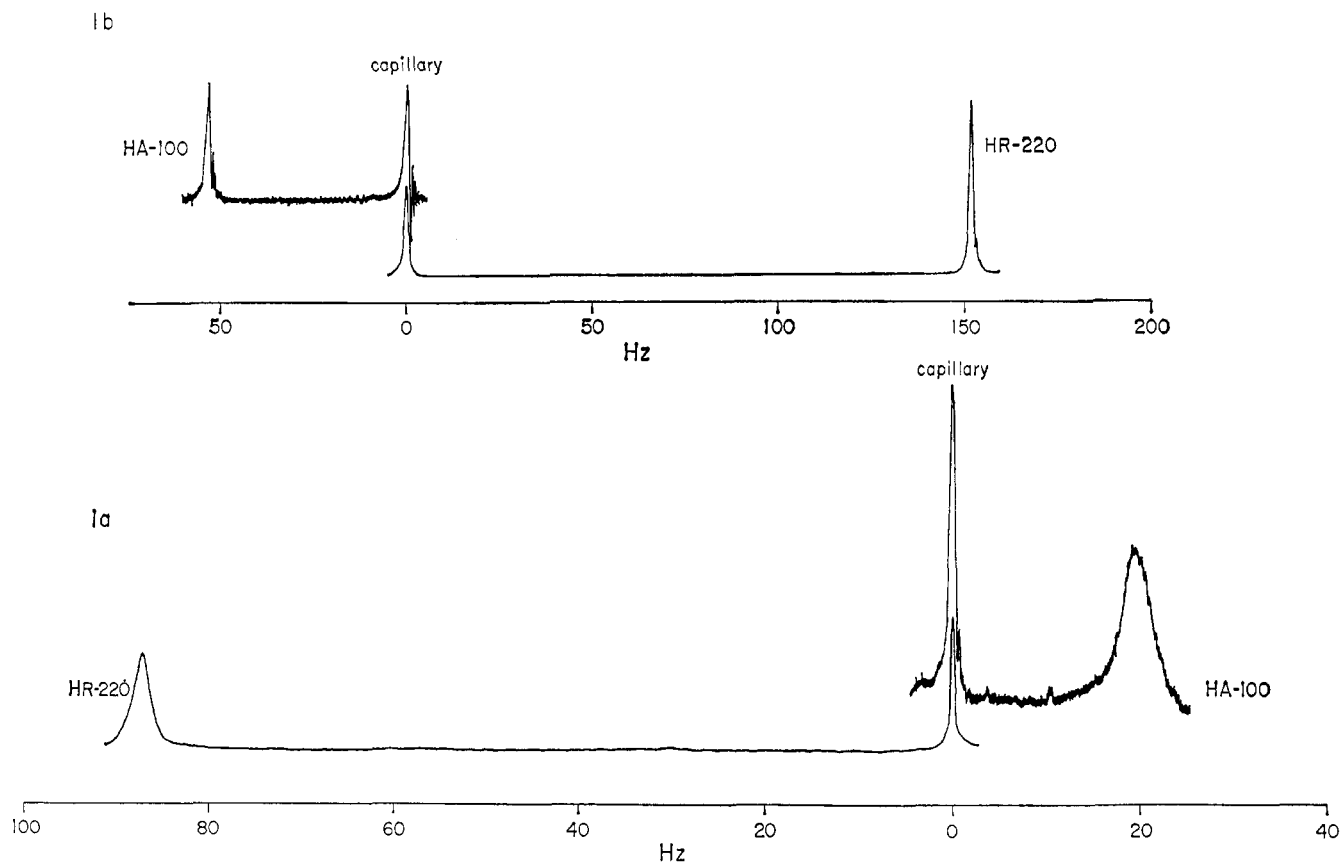


Figure 1. (a) Comparison of effects of DPPH on HA-100 and HR-220 spectra of TMS in CHCl_3 relative to corresponding spectra of undoped solution contained in a capillary. Temperature: 33°C . (b) Comparison of HA-100 and HR-220 spectra of TMS in CHCl_3 relative to neat TMS sealed in a capillary

Note Added in Proof. Subsequent to the submission of this communication, Beconsall *et al.* [J. K. Beconsall, G. D. Davies, and W. R. Anderson, Jr., *J. Amer. Chem. Soc.*, **92**, 430 (1970)] have presented, without explicit experimental proof, equations equivalent to Equations 1' and 4' in this paper.

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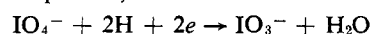
noted the discrepancy between A-60 and HR-220 results of a factor of 2 in the paramagnetic susceptibilities determined using Evan's method (Reference 4) and when Evan's formula was used to interpret the bulk susceptibility shifts.

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Polystyrene Sulfonates as Stable Polarographic Maxima Suppressors in the Determination of Periodate and Cobalt(II)

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POLAROGRAPHIC MEASUREMENT of excess periodate in a kinetic study of the oxidation of certain carbohydrates was hampered by the unwanted oxidation of the conventionally used maxima suppressors (*e.g.*, Triton X-100, gelatin) or by wave-splitting of the two-electron process,



or by severe reduction of the maximum diffusion current (i_d) at low concentrations. As part of a program to develop an

automated polarographic analysis, it became necessary to find a suppressor which was stable to periodate ion over an extended period of time, and which did not reduce the i_d value appreciably. The completely sulfonated polystyrene sulfonic acids (provided as the sodium salt) of narrow molecular weight ranges recently developed by The Dow Chemical Company (Available from Technical Service and Development 2020 Building, Abbott Road Centre, Midland, Mich. 48640) were