Paramagnetic Susceptibility by NMR: The “Solvent Correction” Removed for Large Paramagnetic Molecules

Claude Piguet
Department of Inorganic Chemistry, Sciences II, 30 quai Ernest Ansermet, University of Geneva, CH-1211 Geneva 4, Switzerland

The Evans NMR method (1) for determination of paramagnetic solutes in a diamagnetic solvent is very attractive because a common NMR instrument, often found in a department of chemistry, allows the accurate measurement of paramagnetic susceptibilities (2). Numerous applications have been found in coordination chemistry for the determination of the effective magnetic moments of complexes (3, 4) and for the quantitative description of spin-state equilibria of iron complexes (5).

We wish to draw attention on the problem of the “solvent correction” used in the Evans method, which has been critically reexamined recently by Grant (5) for small paramagnetic molecules in which the diamagnetic contribution is negligible. According to Evans (1), the mass susceptibility χ (cm³ g⁻¹) of the dissolved substance is given by eq 1, where δν is the shift in frequency (Hz) from the value found for the pure solvent (δν > 0 for paramagnetism and δν < 0 for diamagnetism); m is the concentration of the solute (g cm⁻³); S₀ is the shape factor of the magnet (4π/3 for a cylindrical sample in a superconducting magnet (sample axis parallel to the magnetic field) and -2x/3 for an iron core magnet (sample axis perpendicular to the magnetic field)); ν₀ is the operating frequency of the NMR spectrometer (Hz); χ₀ (cm³ g⁻¹) is the mass susceptibility of the pure solvent (χ₀ < 0); and d₀ and dₚ are the densities of the pure solvent and solution, respectively.

\[
\chi = \frac{\delta \nu}{S_0 \nu_0} + \chi_0 + \frac{(d_0 - d_p)}{m} \tag{1}
\]

Introduction of the diamagnetic contribution of the compound χₚdia (cm³ mo l⁻¹) together with substitution of the paramagnetic mass susceptibility (χ) by the paramagnetic molar susceptibility χₚ (cm³ mo l⁻¹) leads to eq 2, where Mₚ is the molecular mass of the dissolved paramagnetic compound (g mo l⁻¹).

\[
\chi_p = \frac{\delta \nu \chi_p\nu_0^3}{S_0 m^3} + \chi_0 \nu_0^3 + \chi_0 M_p \frac{(d_0 - d_p)}{m^3} \tag{2}
\]

Since dₚ tends to dₚ for diluted solutions, many authors (2–4) neglect the term (dₚ - dₚ)/mₚ and the effective magnetic moments μₑff (in Bohr magnetons) can be obtained using eq 3 (6).

\[
\mu_{\text{eff}} \approx 2.828 \sqrt{\frac{T M_p^2}{S_0 m^3}} \left(\frac{\delta \chi_p\nu_0^3}{S_0 + S_1} \frac{\chi_0 M_p}{m^3} \frac{(d_0 - d_p)}{m^3}\right) \tag{3}
\]

However, Grant (5) has recently pointed out that this approximation is erroneous because both the numerator (dₚ - dₚ) and the denominator (mₚ) tend simultaneously to zero for diluted solutions, producing an indeterminate value for the term (dₚ - dₚ)/mₚ whose limit is approximately equal to -1 (5). Grant thus concludes that the third term of eq 2 cancels the second term and that less error is introduced if both terms describing the “solvent correction” are neglected, leading to eq 4.

\[
\chi_p^* = \frac{\delta \nu \chi_p\nu_0^3}{S_0 m^3} \tag{4}
\]

For small molecules, it is certainly justified to neglect the diamagnetic contribution χₚdia (5), but large paramagnetic supramolecular assemblies (7) or biomolecules (8) require a dependable determination of the diamagnetic contribution because the temperature-dependent paramagnetism is often only a small part of the whole signal (8). To solve this problem, the diamagnetic susceptibilities of the appropriate apoprotein (i.e., the derivative of the actual protein in which the paramagnetic ions have been eliminated (9)) or of the analogous supramolecular assemblies where the paramagnetic metal ions have been replaced by appropriate diamagnetic ions must be studied independently. When the Evans NMR method is used for the determination of (i) the paramagnetic moments (χₚ) and (ii) the diamagnetic contributions (χₚdia) of a large molecule in a given solvent (i.e., a paramagnetic protein and its apo-form or a paramagnetic supramolecular assembly and its diamagnetic analogue), the “solvent correction” affects both measurements similarly and is canceled when χₚ is calculated with eq 2.

Let us consider a paramagnetic supramolecular complex of molecular mass Mₚ and its diamagnetic analogue of molecular mass Mdia, where the paramagnetic metal ions are replaced by similar, but diamagnetic, ions. In the first experiment, the diamagnetic contribution is obtained with the Evans method applied to the magnetic susceptibility of the diamagnetic complex according to eq 5 (δνdia ≤ 0). This contribution is then introduced into eq 2 and the paramagnetic susceptibility is measured in a second experiment for the paramagnetic supramolecular complex. The paramagnetic susceptibility (χₚ) is calculated according to eq 6 (δν ≤ 0).

\[
\chi_p^* = \frac{\delta \nu \chi_p\nu_0^3}{S_0 m^3} + \chi_0 M_p \frac{(d_0 - d_p)}{m^3} \tag{5}
\]

\[
\chi_p^* = \frac{\delta \nu \chi_p\nu_0^3}{S_0 m^3} + \chi_0 M_p \frac{(d_0 - d_p)}{m^3} \tag{6}
\]
As the two complexes are very similar, their molecular masses are almost identical \((M^p \cong M^{\text{dia}})\) and the second term of eq 6 tends to zero. For sufficiently large molecules, the diamagnetic contribution is large enough to be detected by the Evans method at concentrations similar to those used for the calculation of paramagnetic susceptibilities. Under these conditions, \(m^p \cong m^{\text{dia}}\) and \(d^p \cong d^{\text{dia}}\); the third term of eq 6 is essentially canceled, leading to the approximate eqs 7 and 8 for the calculation of the paramagnetic susceptibility and magnetic moment, respectively.

\[
\chi_M^p = \frac{1}{\nu_0 S_f} \left[ \frac{\delta \nu^p M^p}{m^p} - \frac{\delta \nu^{\text{dia}} M^{\text{dia}}}{m^{\text{dia}}} \right] 
\]

\[
H_{\text{eff}} = 2.828, \sqrt{\frac{T}{\nu_0 S_f}} \left[ \frac{\delta \nu^p M^p}{m^p} - \frac{\delta \nu^{\text{dia}} M^{\text{dia}}}{m^{\text{dia}}} \right] 
\]

It thus appears that the solvent corrections are canceled if the diamagnetic and paramagnetic contributions can be determined independently using the Evans method and the following criteria: (i) the analogous paramagnetic and diamagnetic compounds display similar molecular masses and (ii) the same conditions are used for both experiments (temperature, concentration, solvent). Recently, Linert et al. (10) have used a related method for the determination of the diamagnetic susceptibilities \(\chi_{\text{dia}}\) of heterocyclic ligands in iron complexes, but they neglect “the solvent corrections” without explicit justifications.

Supramolecular lanthanide assemblies offer a unique possibility for testing this technique since the free-ion approximation (8) still holds for the calculation of paramagnetic moments in complexes of lower symmetry as a result of the significant shielding of 4f orbitals by 5s and 5p electrons (11), and this provides reliable predictions for the magnetic moments of complexes in solution (8). We have recently shown (7, 12) that the segmental ligand \(L\) reacts with Zn(II) and Ln(III) (Ln = Lanthanide = La, Ce, Pr, Nd, Sm, Eu, and Y) to give quantitatively the heterodinuclear triple helical complex \([\text{LnZn(L)}_3]^{3+}\) in acetonitrile (Fig. 1). During the first experiment, the diamagnetic contribution is measured for the diamagnetic complex \([\text{YZn(L)}_3]^{3+}\) in degassed acetonitrile containing 1% TMS as an indicator \((m^{\text{dia}} = 0.0181 \text{ g cm}^{-3}, \delta \nu^{\text{dia}} = -4.4 \text{ Hz at } \nu_0 = 300.075 \times 10^6 \text{ Hz})\), then the paramagnetic moments of Ln(III) (Ln = Ce, Pr, Nd, Sm, Eu) in \([\text{LnZn(L)}_3]^{3+}\) are determined under the same conditions using eq 8 leading to values of \(\mu_{\text{eff}}\) very close to those reported for the free ions (12). This simple example clearly demonstrates that eq 8 is experimentally confirmed and that the solvent correction is removed for large paramagnetic molecules.

**Acknowledgments**

I gratefully thank E. Rivara-Minten for bringing the subject to my attention and for recording NMR spectra. I thank the Werner Foundation for a fellowship and the Swiss National Science Foundation for financial support.

**Literature Cited**