

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

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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 (2, 3) and for the quantitative description of spin-state equilibria of iron complexes (3, 4).

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 ($\text{cm}^3 \text{g}^{-1}$) of the dissolved substance is given by eq 1, where $\delta\nu$ is the shift in frequency (Hz) from the value found for the pure solvent ($\delta\nu > 0$ for paramagnetism and $\delta\nu < 0$ for diamagnetism); m is the concentration of the solute (g cm^{-3}); S_f is the shape factor of the magnet ($4\pi/3$ for a cylindrical sample in a superconducting magnet (sample axis parallel to the magnetic field) and $-2\pi/3$ for an iron core magnet (sample axis perpendicular to the magnetic field) (6); ν_0 is the operating frequency of the NMR spectrometer (Hz); χ_0 ($\text{cm}^3 \text{g}^{-1}$) is the mass susceptibility of the pure solvent ($\chi_0 < 0$); and d_0 and d_s are the densities of the pure solvent and solution, respectively.

$$\chi = \frac{\delta\nu}{\nu_0 S_f m} + \chi_0 + \chi_0 \frac{(d_0 - d_s)}{m} \quad (1)$$

Introduction of the diamagnetic contribution of the compound χ_M^{dia} ($\text{cm}^3 \text{mole}^{-1}$) together with substitution of the paramagnetic mass susceptibility (χ) by the paramagnetic molar susceptibility χ_M^p ($\text{cm}^3 \text{mole}^{-1}$) leads to eq 2, where M^p is the molecular mass of the dissolved paramagnetic compound (g mole^{-1}).

$$\chi_M^p = \frac{\delta\nu^p M^p}{\nu_0 S_f m^p} + \chi_0 M^p + \chi_0 M^p \frac{(d_0 - d_s^p)}{m^p} - \chi_M^{dia} \quad (2)$$

Since d_s^p tends to d_0 for diluted solutions, many authors (2–4) neglect the term $(d_0 - d_s^p)/m^p$ and the effective magnetic moments μ_{eff} (in Bohr magnetons) can be obtained using eq 3 (6).

$$\mu_{\text{eff}} = 2.828 \sqrt{\frac{T M^p}{S_f m^p} \left(\frac{\delta\nu^p}{\nu_0} + S_f m^p \chi_0 - \frac{S_f m^p}{M^p} \chi_M^{dia} \right)} \quad (3)$$

However, Grant (5) has recently pointed out that this approximation is erroneous because both the numerator ($d_0 - d_s^p$) and the denominator (m^p) tend simultaneously to zero for diluted solutions, producing an indeterminate value for the term $(d_0 - d_s^p)/m^p$ 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.

$$\chi_M^p = \frac{\delta\nu^p M^p}{\nu_0 S_f m^p} - \chi_M^{dia} \quad (4)$$

For small molecules, it is certainly justified to neglect the diamagnetic contribution χ_M^{dia} (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 (χ_M^p) and (ii) the diamagnetic contributions (χ_M^{dia}) 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 χ_M^p is calculated with eq 2.

Let us consider a paramagnetic supramolecular complex of molecular mass M^p and its diamagnetic analogue of molecular mass M^{dia} , 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 ($\delta\nu^{dia} \leq 0$). 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 (χ_M^p) is calculated according to eq 6 ($\delta\nu^p \geq 0$).

$$\chi_M^{dia} = \frac{\delta\nu^{dia} M^{dia}}{\nu_0 S_f m^{dia}} + \chi_0 M^{dia} + \chi_0 M^{dia} \frac{d_0 - d_s^{dia}}{m^{dia}} \quad (5)$$

$$\chi_M^p = \frac{1}{\nu_0 S_f} \left[\frac{\delta\nu^p M^p}{m^p} - \frac{\delta\nu^{dia} M^{dia}}{m^{dia}} \right] + \chi_0 (M^p - M^{dia}) \quad (6)$$

$$+ \chi_0 \left[\frac{M^p (d_0 - d_s^p)}{m^p} - \frac{M^{dia} (d_0 - d_s^{dia})}{m^{dia}} \right]$$

As the two complexes are very similar, their molecular masses are almost identical ($M^p \cong M^{dia}$) 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, $m^p \cong m^{dia}$ and $d_s^p \cong d_s^{dia}$; 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.

$$\chi_M^p = \frac{1}{\nu_0 S_f} \left[\frac{\delta\nu^p M^p}{m^p} - \frac{\delta\nu^{dia} M^{dia}}{m^{dia}} \right] \quad (7)$$

$$\mu_{eff} = 2.828 \sqrt{\frac{T}{\nu_0 S_f} \left[\frac{\delta\nu^p M^p}{m^p} - \frac{\delta\nu^{dia} M^{dia}}{m^{dia}} \right]} \quad (8)$$

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 (χ_M^{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 $[\text{LnZn}(\text{L})_3]^{5+}$ in acetonitrile (Fig. 1). During the first experiment, the diamagnetic contribution is measured for the diamagnetic complex $[\text{YZn}(\text{L})_3]^{5+}$ in degassed acetonitrile containing 1% TMS as an indicator ($m^{dia} = 0.0181 \text{ g cm}^{-3}$, $\delta\nu^{dia} = -4.4 \text{ Hz}$ at $\nu_0 = 300.075 \times 10^6 \text{ Hz}$), then the paramagnetic moments of Ln(III) (Ln = Ce, Pr, Nd,

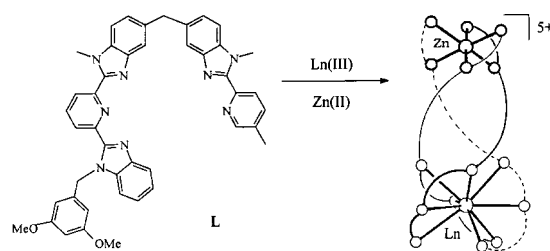


Figure 1. Self-assembly of $[\text{LnZn}(\text{L})_3]^{5+}$ in acetonitrile.

Sm, Eu) in $[\text{LnZn}(\text{L})_3]^{5+}$ are determined under the same conditions using eq 8 leading to values of μ_{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.

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