

Paramagnetic Susceptibility by NMR

The "Solvent Correction" Reexamined

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Chemistry students' first encounter with the topic of susceptibility is usually in the context of the magnetic properties of transition metal complexes. If these are solids, then they may make use of the Gouy and related experimental methods. Although the instrumentation is not particularly expensive, it is specialized. By contrast, Evans' NMR method (1) for paramagnetic solutes in a diamagnetic solvent (e.g., 2–3% aqueous *t*-butanol) is attractive because it uses instrumentation that, although expensive, has so many other applications it may be as widely available.

We wish to draw attention to a misinterpretation of the original paper that has resulted in an error in some subsequent publications on this NMR method. As used by Deutsch and Poling (2) the heart of the Evans method is the following equation for χ , representing the mass susceptibility of the solute.

$$\chi = \frac{3}{2\pi} \cdot \frac{\delta\nu}{\nu_0} \cdot \frac{1}{m} + \chi_0 + \chi_0 \frac{d_0 - d_s}{m}$$

where $\delta\nu$ is the shift in frequency from the value ν_0 for pure solvent; m is the concentration of the solute in g cm^{-3} ; d_0 and d_s are the densities of pure solvent and solution; and χ_0 is the mass susceptibility of the solvent, or $-0.72 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ for the dilute aqueous *t*-butanol.

In the process of converting this to a form appropriate to SI units,

$$\chi = 6 \cdot \frac{\delta\nu}{\nu_0} \cdot \frac{1}{m} + \chi_0 + \chi_0 \frac{d_0 - d_s}{m}$$

with χ_0 now $-9.05 \times 10^{-9} \text{ m}^3 \text{ kg}^{-1}$, we reexamined the assertion that the last, or third, term can often be neglected. This claim is repeated in another paper (3) and in at least three laboratory texts (4–6) that describe this experiment.

Certainly the difference in densities in the numerator will tend to zero as the solutions become more dilute but so also will the concentration in the denominator. Thus, the ratio $(d_0 - d_s)/m$ becomes indeterminate rather than zero. Trial values for these numbers soon confirmed that this ratio could easily be between 0 and -1 . More formally, we considered the following two cases that although not "limits" in the mathematical sense, probably represent extremes between which most practical cases will lie. In both cases, m g of solute of density d are contained in 1 cm^3 of solution of density d_s , that is, in a mass d_s g of solution.

Case 1

Assume that the solute dissolves without an increase in volume, in effect that the solute has zero partial specific or molar volume. The volume of the solvent is therefore 1 cm^3 and its mass is d_0 .

Since masses are additive,

$$d_s = d_0 + m$$

or

$$\frac{d_0 - d_s}{m} = -1$$

Case 2

Assume that the partial specific or molar volumes are the same as in the pure solute, that is, that the volumes of solute, m/d , and solvent $(d_s - m)/d_0$ will be additive. That is,

$$1 = \frac{d_s - m}{d_0} + \frac{m}{d}$$

multiplying by d_0/m gives

$$\frac{d_0}{m} = \frac{d_s}{m} - 1 + \frac{d_0}{d}$$

or

$$\frac{d_0 - d_s}{m} = -1 + \frac{d_0}{d}$$

For a solute that is twice as dense as the solvent the ratio $(d_0 - d_s)/m$ will be -0.5 , and approaches -1 as the solute becomes more dense. In both cases therefore the third term partially or completely cancels the second. Thus, less error will be introduced by neglecting both second and third terms rather than the current practice of neglecting the third term only.

Reexamination of the Original Paper

At this point it is instructive to reexamine what appeared in the original paper by Evans.

For highly paramagnetic substances the last term can often be neglected without serious error (2% for NiCl_2 solutions).

It is the figure in parentheses that is significant. Because two different NiCl_2 solutions were studied, it cannot refer to $(d_0 - d_s)$, which must vary; it seems to have been interpreted to refer to the complete third term. Actually it refers to the value of χ_0 relative to χ , and hence 2% represents an upper limit to the effect of second and third terms combined.

As final proof, consider the results of Chacravarti and Prasad (7) who carried out very precise determinations of the densities of dilute aqueous NiCl_2 solutions at 35°C . They showed that the apparent molal volume, ϕ , of the solute was related to its molarity, c , as follows.

$$\phi (\text{cm}^3 \text{ mol}^{-1}) = 10.0 + 9.6c^{1/2}$$

This leads to the following expression.

$$\frac{d_0 - d_s}{m} = -1 + (7.67 \times 10^{-3})(10.0 + 26.7m^{1/2})$$

In the limit this goes to -0.92_3 , or -0.90_2 and -0.89_4 at the two concentrations (0.081 and 0.162 M) studied by Evans. Thus, a 1.8% error resulting from neglect of the third term can be reduced to one of 0.2% by neglecting both solvent terms. There is no reason to believe that the small

difference in temperatures and the presence of *t*-butanol in both pure solvent and solution will alter these conclusions significantly.

Less error will be introduced by eliminating both terms in χ_0 rather than only the last. Also, the resulting simplification makes it easier to express the molar susceptibility of the species in solution as a function of its molarity. This seems more logical than first calculating the mass susceptibility of the solid solute from which the solution may or may not have been prepared. Thus,

$$\chi_M (\text{m}^3 \text{mol}^{-1}) = \frac{6}{10^3} \cdot \frac{1}{c} \cdot \frac{\delta v}{\nu_0}$$

where c is the molarity in its usual units of mol dm^{-3} .

If one then neglects the diamagnetic contributions within the paramagnetic species, the effective magnetic dipole as a multiple of the Bohr Magnetron can then be approximated to

$$\begin{aligned} \mu_{\text{eff}} &= \left(\frac{1}{10^3} \cdot \frac{18k}{N_0 \mu_0 (\mu_B)^2} \cdot \frac{T}{c} \cdot \frac{\delta v}{\nu_0} \right)^{1/2} \\ &= 7.98 \times 10^{-3} \left(\frac{T \delta v}{c} \right)^{1/2} \quad \text{for } \nu_0 = 60 \text{ MHz} \end{aligned}$$

$$= 0.138 \left(\frac{\delta v}{c} \right)^{1/2} \quad \text{at 298 K}$$

where k is the Boltzmann constant; N_0 is the Avogadro constant; μ_0 is the vacuum permeability; and μ_B is the Bohr magneton.

A somewhat similar approximate equation appears in the paper by Loeliger and Scheffold (8) but the concentration is expressed in mol cm^{-3} , resulting in a factor for 60-MHz operation of 2.522×10^{-4} . (The 2522×10^{-4} that appears in the original is presumably a typographical error.) There is no discussion as to its origin.

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