

A Cautionary Note on the Use of the Evans Method for Magnetic Measurements

A great advantage of the Evans (1) nmr method for the determination of magnetic susceptibility is that measurements are made on the solution phase and thereby supplement the solid state measurements made by the Gouy and Faraday techniques. A recent article in THIS JOURNAL (2) discussed the powerful extension of the technique to the study of solution equilibria involving species with different magnetic moments. Those authors also point out that the use of a variable temperature nmr probe will allow the thermodynamic parameters of the equilibria to be ascertained. Of course an inert paramagnetic solute can be examined in the same way to test the maintenance of the Curie-Weiss law.

In our own work this method has been particularly useful in the study of air-sensitive materials prepared in evacuated nmr tubes. A point of particular interest was whether one of these compounds changed its magnetic moment with temperature. We observed a reasonable susceptibility at room temperature. Variation of the temperature indicated the Curie-Weiss law was in effect ($\mu_{\text{eff}} = 2.84 \sqrt{\chi_m(T - \Theta)}$) and μ_{eff} was essentially constant. However, the observed Weiss constant had an unreasonably large value for that system and the μ_{eff} was likewise lower than expected.

An explanation for this behavior was found in the thermal expansion of the solution and the resulting change in the concentration of the paramagnetic solute as a function of temperature. Correcting for the different density of the solvent at each temperature resulted in the data fitting the Curie-Weiss law with $\Theta = 0$. Likewise the μ_{eff} increased.

To illustrate this we sought to examine a well-known material, the magnetic moment of which had already been studied at various temperatures. Iron acetylacetonate was chosen due to its high susceptibility,

its previous examination (3) and the fact that it is a coordinately saturated monomer in solution.

The plots of $1/\chi_m^{\text{corr}}$ versus T for $\text{Fe}(\text{acac})_3$ in toluene are shown in the figure. Line I is fitted to the data without any corrections (except for ligand and solvent diamagnetism) and line II is fitted to the data corrected for the relative volume change of the solvent and concentration change of the solute. From line I a value of $\mu_{\text{eff}} = 5.50$ BM and $\Theta = 67^\circ$ is obtained by either measuring the slope or fitting the Curie-Weiss law. Treatment of line II gives the values $\mu_{\text{eff}} = 6.05$ BM and $\Theta = 0^\circ$ in agreement with the reported and spin only value of $\mu_{\text{eff}} = 5.92$ BM and the $\Theta = 0$ observed in the solid state.

Experimental

Ferric Acetylacetonate. Prepared by mixing aqueous FeCl_3 with an ammoniacal solution of acetylacetone in a manner exactly analogous to Young's synthesis of the aluminum compound (4). It was recrystallized from hot benzene hexane (mp $180\text{--}181^\circ\text{C}$, reported (5) 179°C).

Susceptibility Measurements. A toluene solution of $\text{Fe}(\text{acac})_3$ (8.38 mg/ml) containing about 5% TMS was placed in an nmr tube along with a capillary containing 5% TMS in toluene. Variable temperature spectra were recorded on a Varian A-60 nmr spectrometer. The density of toluene at various temperatures was taken from the literature (6). The concentration of the solute was calculated for each temperature as

$$M_T = M_{RT}(d_T/d_{RT})$$

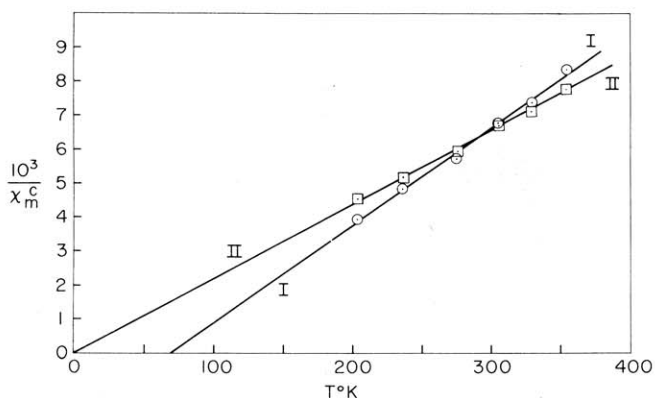
where M_T and M_{RT} are the solute concentrations at temperature T and room temperature, and d_T and d_{RT} are the solvent densities at temperature T and room temperature, respectively. All other diamagnetic corrections are as usual.

Summary

Application of the Evans method for temperature dependent studies of magnetic susceptibility or equilibria will lead to erroneous results unless the variation of the solvent density with temperature is taken into account. For a solvent with a volume change of about 10% for 100°C the error in the slope of the reciprocal susceptibility versus temperature will be about 20–25%. This will result in incorrect values for μ_{eff} , Θ and the thermodynamic parameters in equilibrium studies. Our survey of the literature has not revealed any previous discussion of this correction. In any case, because of the growing use of this method, we feel a cautionary note is necessary.

Literature Cited

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The reciprocal magnetic susceptibility versus temperature observed for $\text{Fe}(\text{acac})_3$ in toluene by the Evans method. Line I describes the uncorrected experimental points and Line II describes those points corrected for the temperature dependent volume changes of the solvent.