Magnetic Titrations by a Nuclear Magnetic Resonance Method

By **D. F. Evans**, Inorganic Chemistry Laboratories, Imperial College, London SW7 2AY

The application to magnetic titrations of an n.m.r. method for determining paramagnetic susceptibilities in solution is described. The technique is tested using the oxidation of ferrocyanide to ferricyanide with bromate, and applied to the titration of the nickel(II) ion with the dithioloxalate anion.

WHEN a reaction (*e.g.*, oxidation, reduction, or complex formation) involves an appreciable change in magnetic susceptibility, a magnetic titration can give not only the magnitude of this change, but also the stoicheiometry of the reaction. The usual Gouy method is very inconvenient for this purpose, although the special Gouy tube developed by Heit and Ryan [1] considerably simplifies the procedure. This paper describes the application to magnetic titrations of an n.m.r. method for measuring paramagnetic susceptibilities in solution.[2] In this method as normally applied an inert reference is present in the solution, and the shift Δf caused by the paramagnetic solute is measured. The magnetic susceptibility χ of the dissolved substance is given by equation (1)

$$\chi = \frac{3\Delta f}{2\pi f m} + \chi_0 + \frac{\chi_0(d_0 - d_s)}{m} \qquad (1)$$

where f is the oscillator frequency, m is the mass of substance in 1 ml of solution, χ_0 is the mass susceptibility of the solvent, d_0 is the density of the solvent, and d_s that of the solution. To determine the atomic susceptibility χ_A of the metal atom in a complex d_s should be measured and a correction for the diamagnetic susceptibility of the ligands applied although an approximate expression for χ_A has been derived which does not require these corrections.[3] However, in a magnetic titration of a metal complex, the diamagnetic contribution of the ligands will remain constant to a high degree of accuracy, and any error involved should be much less than in the usual procedure of estimating these diamagnetic corrections from Pascal's constants. This would be an advantage in systems of biological interest containing a metal atom of variable valency bound to a ligand of very high molecular weight.

When the n.m.r. method is applied to magnetic titrations, a suitable external reference is used as described in the Experimental section, and a dilute solution of the substance under investigation containing an internal reference is treated with successive volumes of a much more concentrated solution of the titrant. If an essentially quantitative reaction occurs, results similar to those given in Figure 1 will be observed. The

---

[1] M. L. Heit and D. E. Ryan, *Analyt. Chim. Acta*, 1963, **29**, 524.

[2] D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

[3] D. F. Evans, G. V. Fazakerley, and R. F. Phillips, *J. Chem. Soc.* (*A*), 1971, 1931.

reaction involved here is (2). In the region where this reaction is occurring, a straight line of appreciable slope

$$6Fe(CN)_6^{4-} + BrO_3^- + 6H^+ \longrightarrow 6Fe(CN)_6^{3-} + Br^- + 3H_2O \quad (2)$$

is found. After completion of the reaction, the results fall on another straight line almost parallel to the x axis. The second straight line will not necessarily have zero slope because of dilution effects and slight differences in the diamagnetic contributions for the metal complex and titrant solutions. However, these effects can be corrected for by extrapolating the second straight line to meet the y axis at Δf_1, as shown. Then, for any metal complex, we have equation (3) where $(\Delta f_1 - \Delta f_0)$

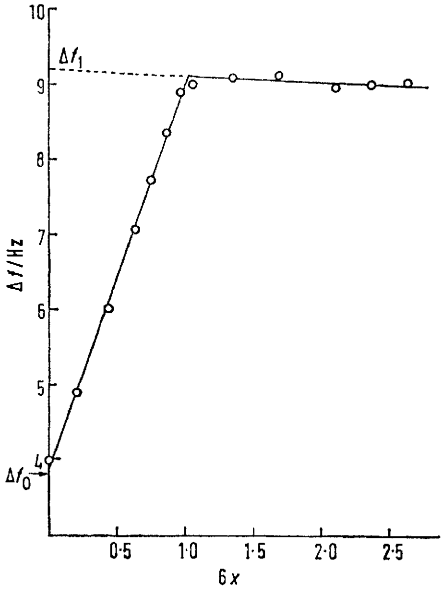

FIGURE 1 Magnetic titration of $1{\cdot}03 \times 10^{-2}$M-$K_4Fe(CN)_6$ in $0{\cdot}3$M-HCl with 6×10^{-2}M-$KBrO_3$. Δf is the difference in chemical shifts of the internal and external references, x is the molar ratio of BrO_3^- added to $Fe(CN)_6^{4-}$ taken

$$\Delta\chi_A = \frac{3(\Delta f_1 - \Delta f_0)A}{2\pi f m_1} \quad (3)$$

is the difference in the two intercepts, A is the atomic weight of the metal, and m_1 is the mass of metal in 1 ml of the initial solution being titrated. If, as in this instance, the metal atom or ion is diamagnetic in either the initial or the final form, then $|\Delta\chi_A|$ is equal to χ_A, the atomic susceptibility of the paramagnetic form. From Figure 1, the Bohr magneton number of $K_3Fe(CN)_6$ is found to be 2·46, in reasonable agreement with the average literature value (corrected for diamagnetism) of 2·40.[4] Also, the intersection of the two straight lines closely corresponds to that expected from the stoicheiometry of the reaction, and the concentrations of the reactants.

This method was then applied to the magnetic titration of $Ni(H_2O)_6^{2+}$ with the dithioloxalate ion $C_2O_2S_2^{2-}$ to give the purple complex ion $Ni(C_2O_2S_2)_2^{2-}$, for which k_1k_2 is *ca.* $10^{9.5}$.[5] The solid potassium salt $K_2Ni(C_2O_2S_2)_2$ has been shown to be diamagnetic,[6] presumably with square planar nickel. The results are in Figure 2. $\Delta\chi_A$ is found to be 4300×10^{-6} at 35 °C, which is close to χ_A for $Ni(H_2O)_6^{2+}$ in $NiCl_2$ solution (4270×10^{-6}).[7] Thus, as expected from the solid-state results, the nickel ion in the complex has a Bohr magneton number of zero. In the region from $x = 0$ to $x = 2$, the data lie approximately on a straight line (Figure 2). This suggests that $k_2 > k_1$ for the $Ni(H_2O)_6^{2+}$–$C_2O_2S_2^{2-}$ system, since the initial formation of the 1 : 1 complex, whether it is paramagnetic as expected, or diamagnetic, would cause deviations from linearity. This is consistent with the spectroscopic data,[5] which were interpreted in terms of a 1 : 2 complex only, and can be attributed to the orbital stabilization associated with spin-paired square planar nickel (*cf.* the similar case of the Fe^{2+}–1,10-phenanthroline system for which $k_3 \gg k_1k_2$).[8]

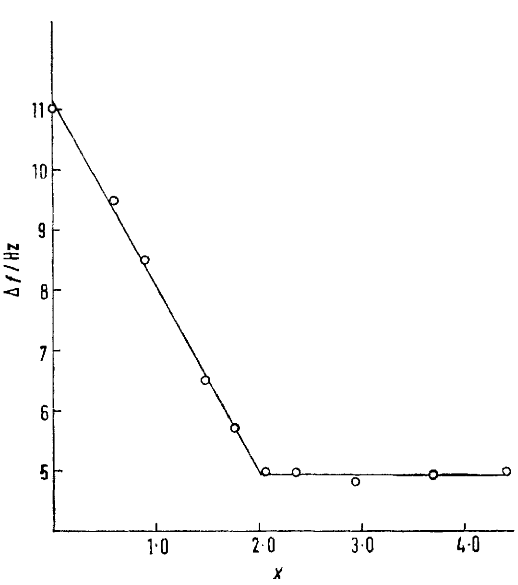

FIGURE 2 Magnetic titration of $6{\cdot}86 \times 10^{-3}$M-$Ni(ClO_4)_2$ with $0{\cdot}61$M-$K_2C_2O_2S_2$, x is the molar ratio of $C_2O_2S_2^{2-}$ added to $Ni(H_2O)_6^{2+}$ taken

EXPERIMENTAL

For aqueous solutions, 3% (w/v) of sodium 4,4-dimethyl-4-silapentanesulphonate was added, and the external reference consisted of a 1 mm o.d. capillary with polytetrafluoroethylene spacers (Nuclear Magnetic Resonance Ltd.) containing a mixture of hexamethyldisiloxane and tetrachloroethylene (31 : 69 v.v.). With diamagnetic solutes, the external reference signal was then 0·04—0·05 p.p.m. to low field of the internal reference, and of comparable

---

[4] G. Foex, 'Diamagnetisme et Paramagnetisme,' Masson, Paris, 1957.

[5] W. A. Deskin, *J. Amer. Chem. Soc.*, 1958, **80**, 5680.

[6] D. P. Mellor and D. P. Craig, *J. Proc. Roy. Soc. N.S.Wales*, 1940, **74**, 475.

[7] H. R. Nettleton and S. Sugden, *Proc. Roy. Soc.*, 1939, *A*, **173**, 313.

[8] H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 1953, 3192.

intensity. For magnetic titrations, this arrangement is preferable to that normally used [2] since with diamagnetic solutes the two reference signals do not overlap and with paramagnetic solutes spinning side bands are considerably reduced in intensity. The n.m.r. tubes were stoppered with rubber serum caps, and the solutions could be deoxygenated with a stream of nitrogen by use of thin hypodermic tubing. The titrant was added from a 10 µl syringe. The spectra were measured at 100 MHz on a Perkin-Elmer R14 spectrometer, with adjustment of the two main homogeneity controls to give sharp and symmetrical signals from both the internal and the external reference.

Potassium dithioloxalate (Eastman Kodak Ltd.) contained a less soluble impurity. It was extracted with water–methanol, precipitated with acetone, and analysed as $BaSO_4$.

[3/1297 *Received*, 19*th June*, 1973]