400. *The Determination of the Paramagnetic Susceptibility of Substances in Solution by Nuclear Magnetic Resonance.*

By D. F. Evans.

The shifts of the proton resonance lines of *inert* reference molecules in solution caused by paramagnetic substances are accurately given by the theoretical espression $\Delta H/H = (2\pi/3)\Delta\kappa$ where $\Delta\kappa$ is the change in volume susceptibility. For aqueous solutions of paramagnetic substances, about 2% of t-butyl alcohol is incorporated, and an aqueous solution of t-butyl alcohol of the same concentration is used as an external reference. Values obtained for the susceptibility of a variety of paramagnetic molecules are in satisfactory agreement with those in the literature. Less than 0·03 ml. of a dilute solution can be studied.

The position of a line in the proton resonance spectrum of a molecule depends on the bulk susceptibility of the medium in which the molecule is situated. For an inert substance (dioxan) in aqueous solution, the shifts caused by paramagnetic ions are given [1] by the theoretical expression [2]

$$\Delta H/H = (2\pi/3)\Delta\kappa \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where $\Delta\kappa$ is the change in volume susceptibility. This is consistent with some earlier work of Phillips, Looney, and Ikeda [3] on the nuclear magnetic resonance spectra of alcohols containing paramagnetic ions, and is in contrast with measurements on mixtures of diamagnetic liquids [4] where higher values of the numerical factor (~2·60) were obtained. A simple method of measuring the paramagnetic susceptibilities of substances in dilute solution is therefore available. Bothner-By and Glick [4] have suggested the use of eqn. (1) with a numerical factor of 2·60 for measuring the susceptibilities of *diamagnetic* substances, but the presence of an empirical factor of doubtful constancy seems to detract from the utility of this method.

For aqueous solutions of paramagnetic substances about 2% of t-butyl alcohol is

---

[1] Evans, *Proc. Chem. Soc.*, 1958, 115.

[2] Dickinson, *Phys. Rev.*, 1951, **81**, 717.

[3] Phillips, Looney, and Ikeda, *J. Chem. Phys.*, 1957, **27**, 1435.

[4] Bothner-By and Glick, *J. Chem. Phys.*, 1957, **26**, 1647.

incorporated as an inert reference substance, and a capillary containing the same concentration of t-butyl alcohol in water is also placed in the nuclear magnetic resonance tube which is spun during the measurement. (The change in the susceptibility of the dissolved compound caused by the t-butyl alcohol will normally be completely negligible.) Two resonance lines will normally be obtained from the methyl protons of the t-butyl alcohol in the two solutions owing to the difference in their volume susceptibilities, with the line from the more paramagnetic solution lying at higher frequencies. The mass susceptibility, χ, of the dissolved substance is then given by the expression

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

where Δf is the frequency separation between the two lines in cycles/sec., f is the frequency at which the proton resonances are being studied, in cycles/sec., m is the mass of substance contained in 1 ml. of solution, χ_0 is the mass susceptibility of the solvent ($-0{\cdot}72 \times 10^{-6}$ for dilute t-butyl alcohol solutions), d_0 is the density of the solvent and d_s that of the solution. For highly paramagnetic substances the last term can often be neglected without serious error (2% for $NiCl_2$ solutions). Acetone or dioxan can also be used in place of t-butyl alcohol or, for non-aqueous solutions, cyclohexane or tetramethylsilane.[5] Alternatively a resonance line of the organic solvent itself can be used as a reference, provided there is no interaction with the solute.

Results obtained for various paramagnetic substances are given in the Table, and are in satisfactory agreement with the literature values.

Mass-susceptibilities in solution at 20° ± 1°.

Substance	Concn. (M) *	$10^6\chi$ calc. from eqn. (2)	$10^6\chi$ (lit.)
$NiCl_2$ †	0·162	34·00 ± 0·2	34·20 ± 0·1 [a]
,, ...	0·081	34·14 ± 0·3	34·20 ± 0·1 [a]
$CuSO_4$	0·0788	9·6	10·1 [b]
$K_3Fe(CN)_6$	0·061	7·67	8·24,[c] 6·32 [d]
$NH_4[Cr(CNS)_4(NH_3)_2]$	0·0152	18·6	17·4 [e]
$Ph_2N{\cdot}N(Picryl){\cdot}$	0·0475 §	2·46	2·07,[f] 2·75,[g] 2·70 [h]

* In 2% aqueous t-butyl alcohol, except for diphenylpicrylhydrazyl § which is in 10% cyclohexane (reference)–90% benzene (v/v). † At 20·0° ± 0·2°.

[a] Selwood, "Magnetochemistry," Interscience, New York, 1956, p. 25. [b] Amiel, *Compt. rend.*, 1941, **213**, 240. [c] Sloth and Garner, *J. Chem. Phys.*, 1954, **22**, 2064. [d] Gray and Birse, *J.*, 1914, **105**, 2707. [e] Berkmann and Zacker, *Z. phys. Chem.*, 1926, **124**, 318 (solid; temp. not stated). [f] Turkevich and Selwood, *J. Amer. Chem. Soc.*, 1941, **63**, 1077 (solid). [g] Müller, Müller-Rodloff, and Bunge, *Annalen*, 1935, **520**, 235 (benzene solution). [h] Ref. *g* (solid).

Care should be taken that the concentration of solute is not too high, otherwise the line from the solution will be too broad. The relative magnitude of this effect varies considerably. Thus it is much smaller for nickel or cobaltous complexes than for cupric or chromic complexes (cf. Conger and Selwood [6]).

One particular advantage of the method described above is that only about 0·2 ml. of solution is required. Less than 0·03 ml. of solution can be measured if the concentration of the reference substance is increased somewhat, and the solution to be examined is placed in a narrow capillary tube. In this case the *reference* solution is contained in the main nuclear magnetic resonance tube which, for small frequency shifts, should preferably be of narrow bore to avoid large differences in the intensities of the two resonance lines. The contribution to the measured susceptibility caused by additional diamagnetic solutes (including ligand molecules) can be eliminated by including an equal concentration in the reference solution.

---

[5] Tiers, *J. Phys. Chem.*, 1958, **62**, 1151.

[6] Conger and Selwood, *J. Chem. Phys.*, 1952, **20**, 383.

EXPERIMENTAL

Measurements were made at 40 Mc./sec. on a Varian V4300B spectrometer. 5-mm. o.d. (3·5-mm. i.d.) spinning sample tubes were used, with loose thin-walled capillary tubes ~2·5 mm. o.d. Precision-bore tubes, with the capillary mounted centrally,[7] were not available but would probably prove advantageous. Line separations were measured by the conventional side-band technique, with a Muirhead decade oscillator. The 50 cycles/sec. mains frequency was also used as a more precise standard with the nickel chloride solutions. The accuracy of this frequency during the time measurements were made was kindly confirmed by an engineer at the local Power Station.

Nickel chloride solutions (from " AnalaR " nickel chloride) were analysed for nickel by precipitation with dimethylglyoxime. $NH_4[Cr(CNS)_4(NH_3)_2],H_2O$ was once recrystallised from water. αα-Diphenyl-β-picrylhydrazyl was prepared as described by Goldschmidt,[8] and twice recrystallized from carbon disulphide. " AnalaR " copper sulphate pentahydrate and " AnalaR " potassium ferricyanide were used directly.

The author thanks Dr. L. Pratt for helpful discussions.

INORGANIC CHEMISTRY RESEARCH LABORATORIES,
IMPERIAL COLLEGE, LONDON, S.W.7.

[*Received, February* 10*th*, 1959.

---

[7] Zimmerman and Foster, *J. Phys. Chem.*, 1957, **61**, 282.
[8] Goldschmidt, *Ber.*, 1922, **55**, 628.