Determination of Volume Magnetic Susceptibility (χ_v) by NMR

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The evaluation of χ_v by NMR has been done using a precision coaxial tubing by Zimmerman[1] or using the method devised by Bernstein and Frei.[2] The former procedure, however, is liable to be affected by the setting of the sample tube in the magnetic field, thereby introducing ambiguity into the measurement.[3,4] The latter involves a difficult arrangement of the noncoaxial tubing. In the present work we have rapidly and easily carried out an accurate determination of the χ_v value by NMR measurements using the microcell devised by Flath[5] (Fig. 1).

The measurements were done on a JNM-4H-100 spectrometer at 22.5±0.2°C, and using an internal lock system at 100 MHz. The chemical shifts were calibrated by means of the built-in frequency counter. The precision of the measurements was ±0.1 Hz. All the reagents were obtained commercially and were purified and dried by usual methods. The microcell was obtained from the Wilmad Glass Co. The sample bulb was filled with hexamethyldisilane (HMDS') up to its neck, and the space around the bulb was filled with the sample liquid or solution. At first the chemical shifts of the sample (δ_1) were measured with the spherical part of the bulb at the center of the receiver coil, using the HMDS' signal from the sphere as the lock signal. Then the bulb was put down to the bottom of the cell and the chemical shifts of the sample (δ_2) were measured by using the HMDS' signal from the cylindrical part of the microbulb as the lock signal. A good linear relation was obtained by plotting the $\delta_1 - \delta_2$ value in ppm against the known values of χ_v[6] for bromoform, chloroform, benzene, and acetone.

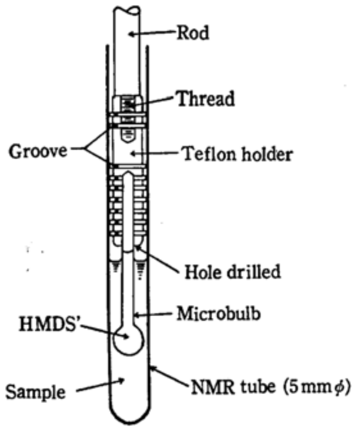

Fig. 1. Illustration of Flath's microcell.[5]

$$\delta_1 - \delta_2 = k[\chi_v(\text{sample}) - \chi_v(\text{HMDS'})] \qquad (1)$$

In Eq. (1) k is the difference between the geometrical constants, $g_{\text{cyl}} - g_{\text{sph}}$, it would be $[2\pi/3-0]=2.094$ for an ideal geometry, but in practice it needs to be determined by calibration.[2,7] In the present case k was shown to be 2.245 from the slope of the linear relation described above. This value was dependent on the shape of the inner bulb, but it was independent of the outer cell and also of the time of measurement if the magnetic field homogeneity had been properly adjusted.

Using Eq. (1) the χ_v values were determined for several organic compounds. The results ($-\chi_v \times 10^6$) are: isobutyl alcohol, 0.623; acetonitrile, 0.527; toluene, 0.620; methanol, 0.523. These values are in good agreement with the results recorded in the literature[6] (0.623, 0.531, 0.620 and 0.527 respectively). The interpolation of the above plots to $\delta_1 - \delta_2 = 0$ shows that χ_v is -0.585×10^{-6} cgs unit for HMDS'; this value has not previously been known, though it can be evaluated to be -0.568×10^{-6} using the gross estimate from Pascal's constant. The relative standard deviation in this technique is about 1.5%.

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