SHORT COMMUNICATIONS

A New Method for the Determination of the Volume Magnetic Susceptibility by NMR

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The determination of the volume magnetic susceptibility (χ_V) by NMR have been done by several workers using a special sample tube.[1-3] In the present work we have developed a new NMR method for determining the χ_V by the use of precision coaxial tubing (Wilmad Glass Co., inside diameters: inner tube, 1.3 mm; outer tube, 4.2 mm) and an NMR shift reagent.

The measurements were carried out on a JNM-4H-100 Spectrometer (100 MHz) at 22.5±0.2°C using an internal locking system. All the organic chemicals were obtained commercially, and they were purified and dried by the usual method. A solution of the shift reagent, Eu(fod)$_3$, in CCl$_4$ containing hexamethyldisiloxane (HMDS) was placed in the central capillary of the coaxial cell, and the sample of interest in the surrounding annulus. After optimizing the performance of the spectrometer and minimizing the intensity of the spinning sideband, the spectrum was measured using the HMDS signal from the inner tube as a lock signal. The signal of the sample in the outer tube is accompanied with fairly strong sidebands, as is illustrated in Fig. 1. The spacing of the bands is twice the spinning rate. The intensities of these sidebands increased with decreases in the spinning rate and in the χ_V of the sample in the surrounding annulus and with an increase in the concentration of Eu(fod)$_3$ in the central capillary. The peak height intensity of the first pair of sidebands(I) increased linearly with an increase in the reciprocal of the spinning rate (Fig. 2). When the intensities at a certain spinning rate are deduced from the results shown in Fig. 2 and plotted against the known values of χ_V[4] for acetone, chloroform, and bromoform, a good linear relation is obtained. The relation at the spinning rate of 30 Hz is as follows:

$$I = -890000\,\chi_V - 0.068 \qquad (1)$$

Fig. 1. NMR Spectrum of benzene in precision coaxial tubing.
Inner tube: 18.3(wt/vol%) solution of Eu(fod)$_3$ in CCl$_4$ and HMDS (1 : 1 vol/vol).
Outer tube: benzene.
Spinning rate: 23.2 Hz.

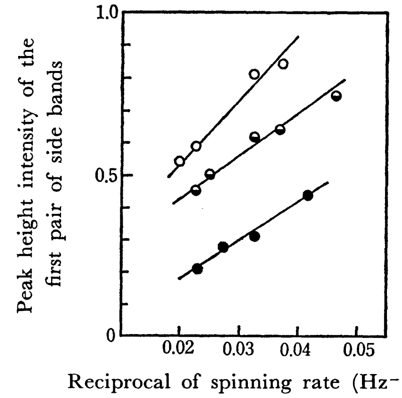

Fig. 2. The intensities of the first pair of sidebands at various spinning rates.
○: Bromoform, ◒: Chloroform, ●: Acetone

Using Eq. (1), the χ_V values of organic compounds can be determined. Some of our results ($-\chi_V \times 10^6$) are: acetonitrile, 0.540; *o*-xylene, 0.661; ethylbenzene, 0.639; benzene, 0.611. These values agree well with those recorded in the literature[4] (0.534, 0.644, 0.634, and 0.611 respectively). Similar results were obtained by placing a solution of Pr(fod)$_3$ or of cupric nitrate in the central capillary. However, on the Varian 220 MHz spectrometer, in which the direction of magnetic field was along the axis of sample spinning, such strong sidebands as are shown in Fig. 1 were not observed and the measurement of χ_V by this method could not be done.

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