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HIGH RESOLUTION NMR MEASUREMENT UNDER HIGH PRESSURE AND PRESSURE DEPENDENCE OF THE PROTON CHEMICAL SHIFTS

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The high resolution proton nmr spectra of a liquid sample under the pressures up to 1650 atm. were obtained at room temperature on an ordinary 60 MHz high resolution spectrometer. Explanation of the handy-type equipment for the experiment and some observations on the pressure dependence of chemical shifts were reported.

There may be two main ways in realizing the high pressure-high resolution nmr measurement. One is to utilize the pressure resistive probe, as has been used for the high pressure broad line nmr and nqr experiments.[1,2] This was done recently by Wilbur and Jonas who used an anti-pressure probe made of Ti-alloy, employing the Fourier transform technique to establish the high resolution ^{19}F-nmr measurements of organic liquid sample.[3] The other way to the high pressure measurement is to use the pressure resistive nmr cell. This technique does not require any modification of the nmr probe; the high resolution experiment can be carried out on an ordinary high resolution nmr spectrometer. The present communication describes a convenient device for the high pressure nmr in the glass made anti-pressure nmr cell and gives some observations on the pressure dependence of the proton chemical shifts. The experiment has been carried out independently[4] from Wilbur-Jonas' work and the technique which uses the anti-pressure glass cell having flexible fine glass capillary does not seem to have been tried as yet in the field of high pressure experiment up to near 1700 atm.

Figure 1 illustrates schematically the employed setup for the present nmr measurement. The sample container (S) having a flexible fine capillary of 0.1-0.5 mm O.D. and ca. 100 cm length and a mercury container (MC) with a piezometer capillary(PZ) were made by drawing out a usual laboratory glass ($\alpha = 5\times10^{-6}$/deg) tube with O.D./I.D. = 3.5. Every one of the parts was etched inside and outside by dilute hydrogen fluoride solution and was coated outside with a collodion lacquer. The end, 5-10 mm in length, of the capillary from (S) was kept uncovered with the lacquer. About 1 ml of mercury followed by 0.004 ml of ether was introduced into (MC) and (PZ) through the very fine capillary (SP) which was subsequently sealed by a micro burner, leaving the very small air space at this point. In the similar manner, (S) was filled with 0.02 ml of sample solution backed by a little quantity of mercury at the end of the capillary. The uncovered part of the capillary was then inserted into the end of (MC) and was fixed there

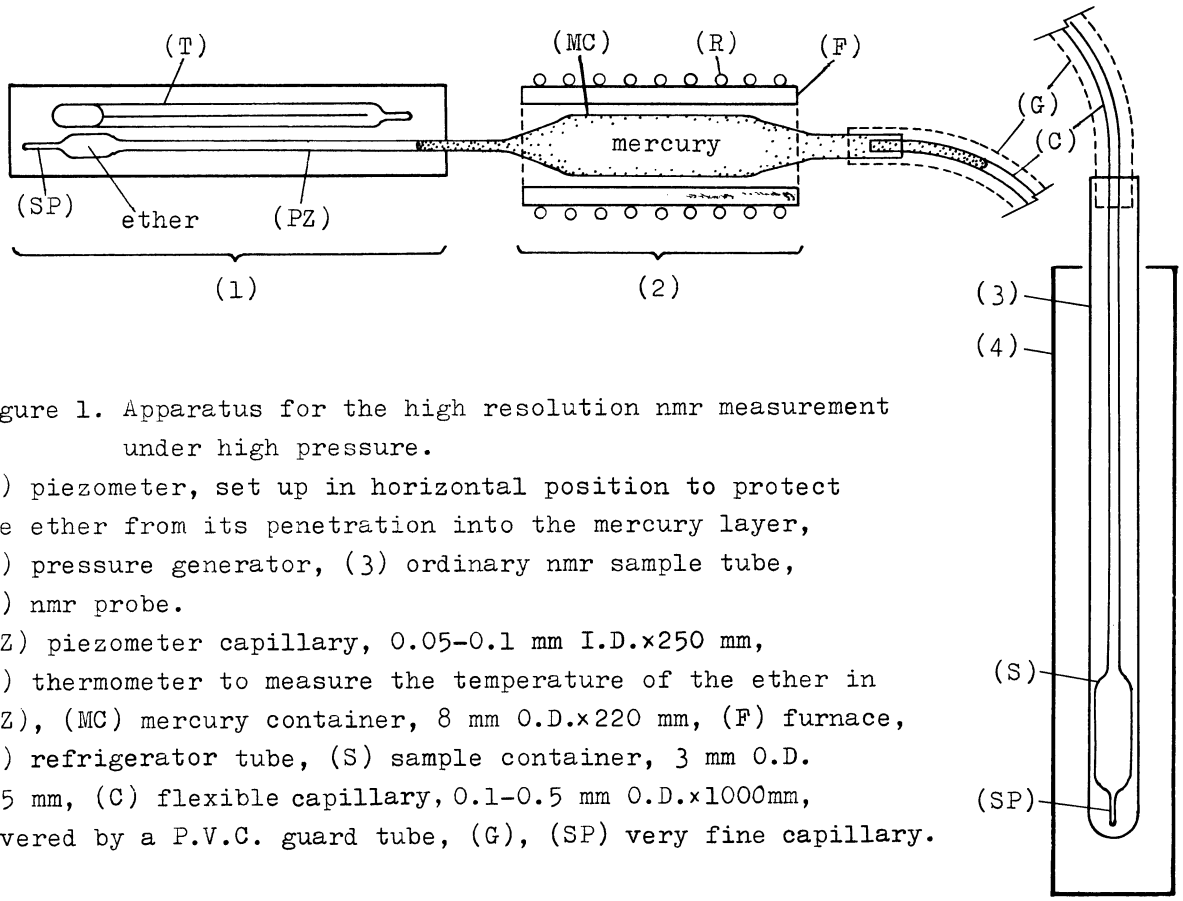

Figure 1. Apparatus for the high resolution nmr measurement under high pressure.
(1) piezometer, set up in horizontal position to protect the ether from its penetration into the mercury layer, (2) pressure generator, (3) ordinary nmr sample tube, (4) nmr probe. (PZ) piezometer capillary, 0.05-0.1 mm I.D.×250 mm, (T) thermometer to measure the temperature of the ether in (PZ), (MC) mercury container, 8 mm O.D.×220 mm, (F) furnace, (R) refrigerator tube, (S) sample container, 3 mm O.D. ×25 mm, (C) flexible capillary, 0.1-0.5 mm O.D.×1000mm, covered by a P.V.C. guard tube, (G), (SP) very fine capillary.

using an epoxy adhesive. While introducing the mercury into (MC) and hardening the adhesive, (MC) was cooled to near 0°C by circulating cold alcohol through the refrigerator tube (R).

In operating the system, (MC) was heated to a constant temperature varying from 25°C to ca. 120°C in an electrical furnace (F). Thus the thermal expansion of the mercury compresses the liquids in the closed system (PZ-MC-S). The resulting contraction of the ether was precisely measured in the calibrated capillary tube (PZ) from which the pressures of the system could be found using the known P-V-T relation of ether.[5] The capillary (SP) at the end of the piezometer was drawn out very finely so that the volume of the air space remained in it was negligibly small and was permitted to be neglected in determining the compression volume of the ether. The pressure expansion of the piezometer, however, could mislead the measurement of the compression volume and hence of the internal pressure. Approximating the elastic cylinder model[6] with O.D./I.D.=3.5 having a Young's modulus of 7×10^3 kg·mm^{-2} and a Poisson's ratio of 0.2[7] to the present piezometer, the expansion, $\Delta V/V$, at the internal pressure, P atm., can be calculated as

$$\Delta V/V = 0.4\times10^{-5} P$$

and as a first approximation, as

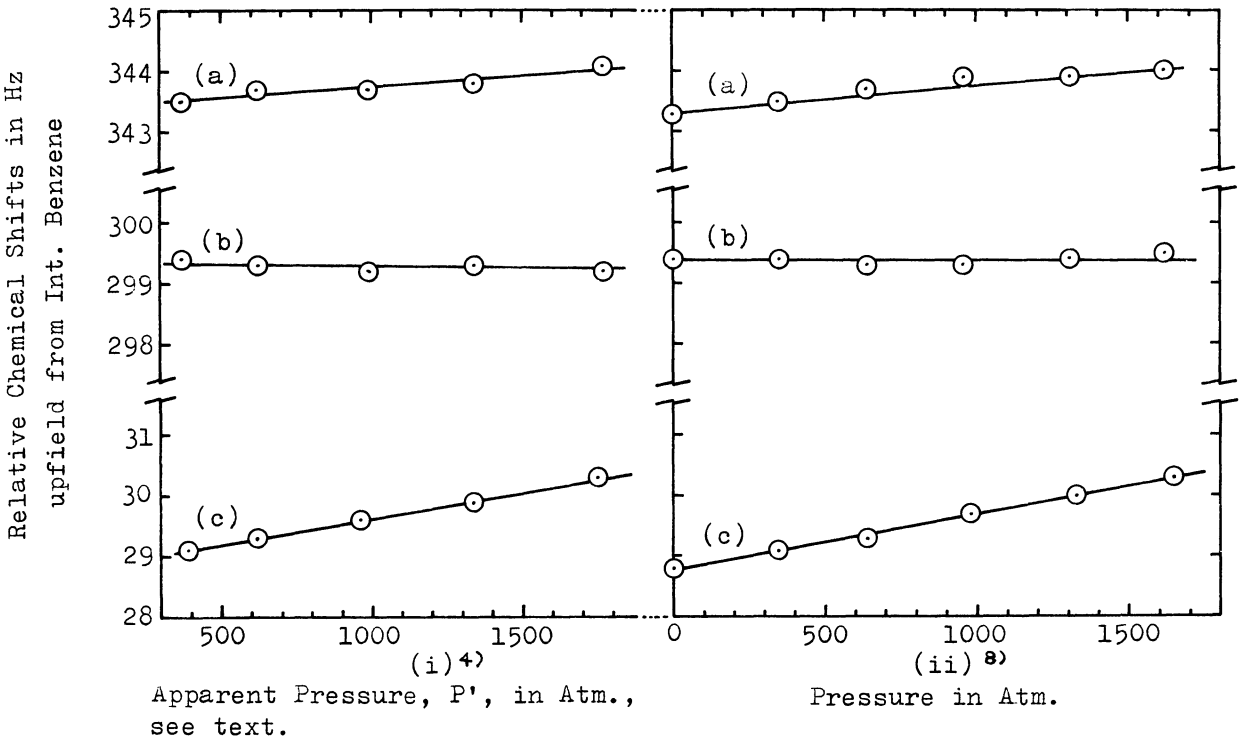

Figure 2. Pressure dependence of the chemical shifts of (a) cyclohexane, (b) methyl protons of mesitylene, and (c) ring protons of mesitylene.

$$\Delta V/V \simeq 0.4\times10^{-5} P'$$

where P' denotes the apparent pressure estimated from the uncorrected contraction volume of the ether. Based on this calculation, the true pressure P was supposed to be approximately 5%, 7%, 8%, and 10% less than the apparent pressure P' of 500 atm., 1000 atm., 1500 atm., and 2000 atm. respectively.

A solution containing 47.5 mole % of benzene and mesitylene and 5.0 mole % of cyclohexane was used as the nmr sample. Although the sample spinning was not attainable with this setup of the apparatus, the very small sectional area of the sample solution helped to perform the high resolution measurement (for the internal benzene, $\Delta\nu_{h/2} = 0.8$-1.0 Hz was preserved in this experiment). Prior to a measurement at a fixed pressure, the temperature was directly read in a thermometer inserted into the liquid paraffin in the nmr tube settled in the probe. Thus the temperature of the sample under the nmr condition was estimated to be maintained at 26.5±1°C throughout the experiment. The chemical shifts were determined versus internal benzene by the usual side band technique. The reproducibility of the observed chemical shifts was ±0.1-0.2 Hz.

Figure 2 (i) shows the observed chemical shifts relative to the internal benzene plotted against the pressures experienced by the sample. The validity of the present results was further checked by the experiment up to 1650 atm. at 28.5-29.0°C for the same sample, carried out in the high pressure glass cell (3 mm O.D.×30 mm, similar to (S) with (C) in Figure 1) connected with a nozzle

mounted to the ordinary high pressure system consisting of 3000 kg/cm^2 Bourdon gauge[9] and hand pressure pump. The reproduced result, Figure 2 (ii), shows that the present observations are evidently correct and valid.

As may readily be seen from Figure 2, the protons (a), (b), and (c) behave differently in accepting the pressure effect. For the moment it can only be said that the different pressure dependence of the proton chemical shifts observed here might arise from the variation in the nature of the protons interacting with the surrounding molecules.

It may be pointed out that the present system to generate and to estimate the high pressure had an advantage, besides its evident convenience and inexpensiveness, that the damage and hazard caused by the explosion of the high pressure system was held to be minimum because of its small internal volume — and hence its small internal energy at high pressure. The inevitable uncertainty, however, in evaluating the pressure expansion of the piezometer yielded a difficulty to determine the precise internal pressure. Further experiments on the various samples having a much larger pressure dependence of chemical shift as well as coupling constant are being carried out using the high pressure glass cell connected with Bourdon high pressure gauge and hand pressure pump and more extensive discussion will be reported in future.

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4) The experiment was carried out in December, 1970. Presented at the 26th Annual Meeting of the Chemical Society of Japan, Hiratsuka, April, 1972.
5) "International Critical Tables", 3, Mcgraw-Hill, New York, (1928), p 42.
6) "High Pressure Technology and Its Application", ed. by The Society of Materials Science, Japan, Maruzen, Tokyo, (1969), Chapt. 3.
7) The data were kindly furnished by Professor Shoji Tsuchihashi of Kobe University.
8) Based on the experiment with Bourdon gauge and hand pressure pump, undertaken in this summer.
9) Calibrated with a 50000 psi Heise gauge which is accurate to ±0.1 %. The author wishes to thank Professor Kaoru Makita of Kobe University for the equipments and helpful suggestions.

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