ACTA CHEMICA SCANDINAVICA 27 (1973) 1–4

A New Method for Measuring Ultrasonic Velocity

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A new cell has been developed for the investigation of ultrasonic velocities. It makes use of a quartz crystal through which a small hole has been bored. The sound velocity in a liquid placed into this hole can be determined by a comparison method from the frequency shift of the resonance peak of the crystal. The test cell has been specially designed for small quantities of liquid (0.2 ml) and to be used at low frequencies (250 kHz).

The ultrasonic relaxation technique has been extensively used to investigate the rates and mechanisms of very fast chemical reactions. Several investigations have been concerned with reactions of biochemical importance, hydrogen bond formation,[1–6] micelle formation,[7,8] and polymer conformation,[9–11] for example, having been studied. A general conclusion of these seems to be that to test a proposed mechanism measurements at low frequencies are desirable.

The resonance technique recently developed[12] can in principle be used to determine sound absorption coefficients and sound velocities at such low frequencies (200 kHz – 1 MHz) and, although there are still certain technical difficulties, the cells designed so far have permitted these determinations to be made. However, measurements at 200 kHz require at least 40 ml of sample, a necessity which, in particular, prohibits the investigation of several synthetic macromolecules which could be studied as models for biological systems.

In this paper a new cell which can be used in the application of the resonance technique is presented. It requires only 0.2 ml of sample and can be used for measurement of ultrasonic velocities at low frequencies.

THEORY

The resonating cavity usually consists of two quartz crystals with the sample between. Standing waves are established in this cavity and a resonance curve is then recorded by measuring the amplitude of the sound wave transported through the cell as a function of its frequency. From this curve the sound absorption coefficient can be obtained. The quality factor, Q, which is

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obtained from the 3 dB point of the resonance curve, is related to the sound absorption coefficient. The sound velocity is determined from the difference between two successive resonance frequencies.

There are several technical difficulties associated with the construction of satisfactory cells. It is important that the quality factor which is determined is mainly due to the sample. This requires that the two quartz crystals oscillate freely and consequently are not coupled to the cell. Furthermore the interpretation of the measurements is based upon the assumption of plane waves so this imposes certain restrictions on the size of the crystals. A measurement at 200 kHz requires a quartz diameter of at least 6 cm. In the past the problems have been partially overcome by mounting big crystals in the cell with soft

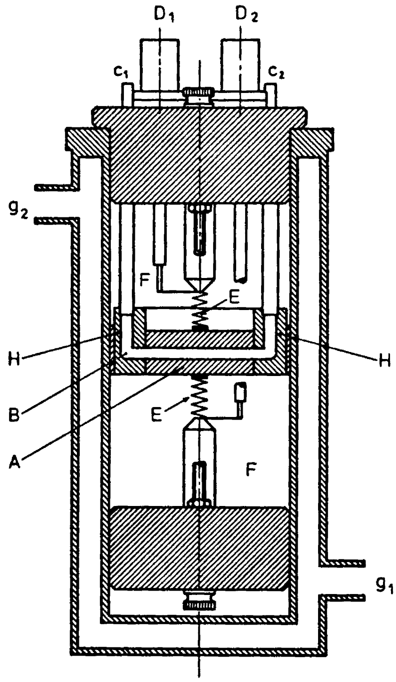

Fig. 1. The resonance cell. A: The x-cut quartz cylinder with a diameter of 3 cm and a basic frequency of 272 kHz. The cylinder is gold plated on both sides. B: The hole (diameter 0.15 cm) which penetrates the crystal and in which the sample is placed. C_1 and C_2: Input and output of sample. D_1 and D_2: Coaxial connections. E: Spring contacts. F: Cavity filled with air. G_1 and G_2: Water jacket.

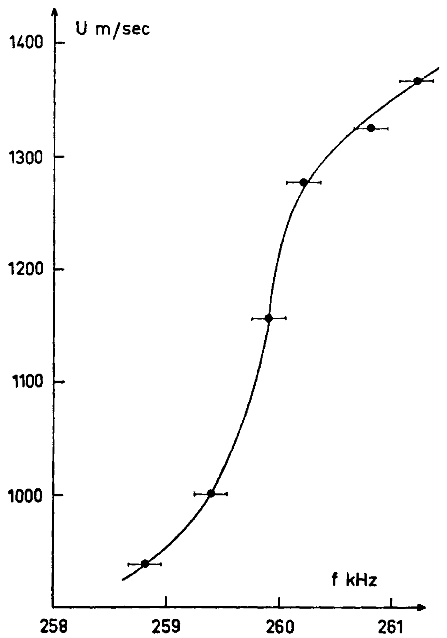

Fig. 2. The relationship between the velocities of the different samples and the resonance frequency of the quartz crystal inside which the samples are placed. The samples used are carbon tetrachloride, chloroform, acetone, cyclohexane, benzene, and dioxane.

The resonance frequency of the cell is measured by means of a set up from Wandel und Goltermann, Wobbelmessplatz, WM-50.

glue. Unfortunately, however, the sample is then in close contact with the glue so that several important organic compounds cannot be used as solvents. In addition the size of the crystals necessitates about 40 ml of sample.

THE NEW METHOD

The method proposed here involves the use of a single x-cut quartz crystal. The lowest resonance frequency for this crystal is given by

$$f = U/2l \tag{1}$$

where U is the sound velocity in quartz and l is the thickness of the crystal. A crystal with a lowest resonance frequency of 272 kHz has been successfully used. Through this crystal a small hole perpendicular to the direction of particle motion has been made. This hole decreases the lowest resonance frequency of the crystal in a complicated manner. It is apparent, however, that the observed decrease is related to the velocity of sound in any liquid placed in the hole. A suitable hole requires only 0.2 ml of sample liquid. Fig. 1 shows the detailed cell design. Before use, a calibration curve such as that shown in Fig. 2 must be plotted. By comparing the resonance frequency of the crystal with a sample and a reference liquid placed in the hole, respectively, the velocity of sound for the sample can be calculated. With the cell described it is possible to measure the sound velocity with a reproducibility of 0.5 %; however, the accuracy may be considerably improved by using a differential cell using two identical crystals.

Measurements at higher frequencies (the odd harmonics) may be carried out although the frequency shift observed decreases the higher the odd harmonics used.

CONCLUSION

A new method which permits measurement of the velocity of sound at low frequencies (250 kHz) in very small samples (0.2 ml) has been developed. The method requires a single x-cut quartz crystal in which a small hole containing the sample has been made. This causes a shift in the normal resonance frequency of the quartz crystal. After suitable calibration this shift can be employed to calculate the sound velocity. Further work improving the performance of the cell is in progress.

Acknowledgement. The authors express their appreciation to professor Thor A. Bak for helpful discussions and to *Statens naturvidenskabelige Forskningsråd*, Denmark, for financial support.

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Received June 15, 1972.