CHEMISTRY LETTERS, pp. 327-329, 1981.

X-RAY DIFFRACTION STUDY OF LIQUID METHANOL

Masami TANAKA[*], Keiko NISHIKAWA[††], and Tsunetake FUJIYAMA[†]
[*]Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo 158
[††]Department of Chemistry, Faculty of Science, Gakushuin University, Mejiro, Toshima-ku, Tokyo 171
[†]Institute for Molecular Science, Okazaki 444

X-ray diffraction intensity measurements of liquid methanol were carried out by use of an energy-dispersive X-ray diffractometer. No apparent maximum due to hydrogen bonded oxygen-oxygen interference was detected in the electronic distribution function. Our diffraction intensity curve and distribution function are consistent with Harvey's results, but in contradiction to those of Wertz and Kruh.

It is expected that structural correlation exists in liquids in which molecules can form strong hydrogen bonds. We investigated the effect of the hydrogen bond on the structure of liquid methanol by using an energy-dispersive X-ray diffractometer.1)

Wertz and Kruh2) and Harvey3) already measured the diffraction intensity from liquid methanol by use of an angle-dispersive X-ray diffractometer. There are some differences between these two results. (a) In Harvey's radial distribution function at 25°C, there exists no apparent peak corresponding to the oxygen-oxygen correlation which must be caused by the hydrogen bond formation. On the other hand, there is an apparent maximum due to the oxygen-oxygen interference at $r = 2.7$ Å in Wertz and Kruh's result. (b) Wertz and Kruh obtained several peaks in their scattering intensity curve, while Harvey observed only one apparent peak at $s = 1.7$ Å^{-1} ($s = 4\pi\sin\theta/\lambda$, 2θ: scattering angle, λ: wavelength). (c) In the scattering intensity curve, a shoulder peak exists on the small s-value side of the main peak in Harvey's result, while it is not found in Wertz and Kruh's result. In view of the existence of hydrogen bond formation, Wertz and Kruh's result may be reasonable. However, the differences between two results are too large. So it is desirable to reinvestigate liquid methanol by X-ray diffraction method.

Details of the apparatus and procedure have been reported elsewhere.1) The scattering intensity was measured at the scattering angles (2θ) of 2.3, 4.3, 8.3, 18.0, and 30°; these angles correspond to the range of s-values from 0.3 to 8.0 Å^{-1}. Myler films (20μm thick) were used as windows. The thickness of the sample was 0.3 cm. Measurements except for that of 30° were carried out by the transmission method. The scattering intensity from Myler film of the sample holder and that from air was measured and subtracted from the total scattering intensity. Absorption correction was made by use of observed absorption coefficients.

The observed total intensity corrected for absorption is shown in Fig. 1.

There are one peak at s = 1.7 Å^{-1} and one shoulder at s = 0.8 Å^{-1}. This result is almost similar to Harvey's result ((b), (c) in the previous paragraph). If there were several peaks in the scattering intensity curve as detected by Wertz and Kruh, we could obtain easily those peaks, because our result obtained by an energy-dispersive method can hardly be disturbed by the fluctuation in source current of the X-ray tube and the resolution of s-values of our diffractometer is high enough. Moreover, by the use of the transmission method, the intensity data can be obtained more accurately, especially for small s-value region. Therefore, there seem to be some systematic errors in Wertz and Kruh's measurement.

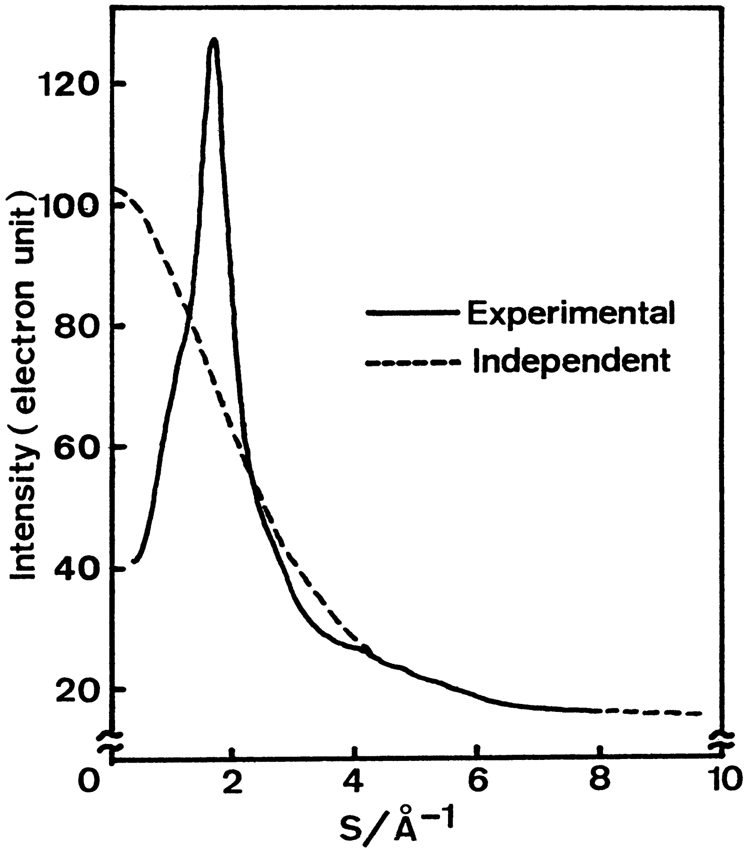

Fig. 1. Observed total coherent intensity and calculated one assuming that atoms are independent.

In our electronic radial distribution function there is no definite peak between 2 Å and 3 Å due to hydrogen bonded oxygen-oxygen interference, as shown in Fig. 2. We think this result means that various distances exist in hydrogen bonded oxigen-oxigen pairs. It is interesting, therefore, that Harvey obtained a well defined peak at about 2.7 Å in his radial distribution function of liquid methanol at -75°C, while he did not observe it at room temperature.$^{3)}$ It seems likely that at room temperature thermal motion of the molecules prevents hydrogen bond formation at a fixed distance.

There exists structural correlation as far as 12 Å in the radial distribution function of methanol at room temperature. This length is about three times the molecular diameter. In carbon tetrachloride there exists correlation as far as 25 Å,$^{1)}$ which is five times the molecular diameter of carbon tetrachloride. Correlation thus holds over a longer distance in carbon tetrachloride than in methanol. This result means that hydrogen bond formation in methanol does not necessarily contribute to structure formation at long distances.

Simulation studies were carried out, but there has been no model which explains the measured intensity curve of liquid methanol. So search for a satisfactory model on liquid methanol is left for future study involving experiments at low temperature.

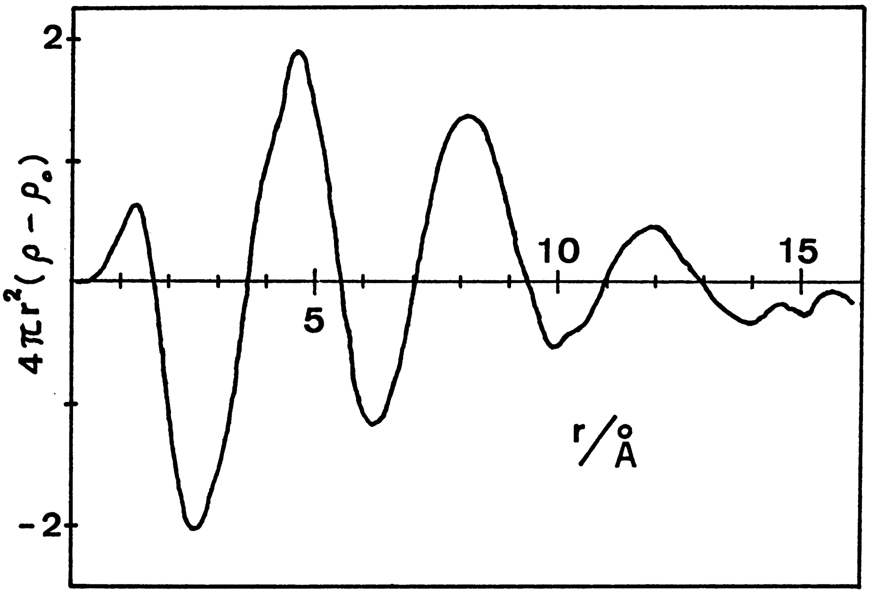

Fig. 2. Electronic radial distribution function from which the bulk density was subtracted.

References:

1) Y. Murata and K. Nishikawa, Bull. Chem. Soc. Jpn., 51, 411 (1978).

2) D. L. Wertz and R. K. Kruh, J. Chem. Phys., 47, 388 (1967).

3) G. G. Harvey, J. Chem. Phys., 6, 111 (1938).

(Received December 25, 1980)