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Fourier Analysis of Liquid Methyl Alcohol*

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X-ray diffraction curves for liquid methyl alcohol have been obtained at 25°C and -75°C with monochromatic Mo $K\alpha$ radiation out to $(\sin \theta)/\lambda = 1.2$. At -75°C there is much greater detail in the diffraction curve than is observable at the higher temperature. Five diffraction rings are visible on the film. Fourier analyses of these intensity curves lead to radial atom distribution functions which are interpreted in terms of Zachariasen's picture of the molecular arrangement in liquid methyl alcohol. The results are distinctly favorable to Zachariasen's picture.

INTRODUCTION

ZACHARIASEN has recently¹ given an interesting picture of the molecular configuration in liquid methyl alcohol. In support of this picture he uses the x-ray diffraction data of Stewart and Morrow² and subjects them to a Fourier analysis. The results obtained, although not too unsatisfactory, leave much to be desired in the way of direct interpretation. There are several reasons for this. First, Stewart and Morrow in their study of the normal alcohols were mainly interested in the position of the principal diffraction peak and the scattering at small angles, and hence did not measure the scattering out to very large angles; further, they did not use strictly monochromatic radiation. Again, the effects of intermolecular interference

rapidly decrease in importance except at small angles of scattering as the temperature of the liquid is raised. Although Dželepov³ has recently measured the scattering from several liquids, including methyl alcohol, with monochromatic radiation, a quantitative interpretation of his results is complicated by his method of measurement and he, too, did not measure the scattering to sufficiently large angles. In the present investigation these defects have been as far as possible remedied.

EXPERIMENTAL

The source of radiation used (Mo $K\alpha$) was a demountable tube with line-focus filament, a simplified modification of the tube described by Dershem.⁴ The tube was very compact, occupying a space of only two by two by ten inches and could be run at an input of 1500 watts continuously. The Mo $K\alpha$ lines were reflected from a rocksalt crystal mounted on the camera and

* A preliminary account of some of the results here reported was given at the Washington Meeting of the American Physical Society in April, 1937. See Phys. Rev. **51**, 998 (1937).

† Now at the College of the City of New York.

¹ W. H. Zachariasen, J. Chem. Phys. **3**, 158 (1935).

² G. W. Stewart and R. M. Morrow, Phys. Rev. **30**, 232 (1927).

³ B. S. Dželepov, Physik. Zeits. Sowjetunion **11**, 157 (1937).

⁴ E. Dershem, Rev. Sci. Inst. **7**, 86 (1936).

placed close to the tube window. The radiation was quite intense and even after passing through the collimating system of the camera the reflected beam could be seen on a fluorescent screen with the room lights on. A free stream of alcohol was used as a sample, the method being essentially the same as that of Katzoff⁵ except that a small "Fountainette" pump was used to

circulate the alcohol. In order to prevent air scattering a stream of hydrogen or helium was passed through the camera continuously throughout the exposures. Fifteen to twenty hour exposures were found to be sufficient if the crystal had been recently polished.

The stream of alcohol flowed from a nozzle accurately centered on the camera (radius 5.43 cm). The radius of the stream was about 0.17 cm and the rate of flow was adjusted so that no turbulence occurred. The stream when observed through a microscope appeared to be a smooth stationary cylinder. The alcohol used was about 99 percent CH₃OH, the remainder being mostly water. A series of pictures was taken at room temperature (25°C). The films were microphotometered and converted to intensities in the usual way. When corrected for polarization and reduced to electron units they give the intensity per molecule as a function of $(\sin \theta)/\lambda$. The absorption factor varied by less than one percent throughout the entire angular range and so was assumed constant. Fig. 1a shows the intensity curve so obtained. It will be seen that beyond $(\sin \theta)/\lambda = 0.5$ the observed scattering is practically indistinguishable from the independent scattering curve. The observed scattering curve was then subjected to a Fourier analysis. Carbon and oxygen are sufficiently different in scattering power to make it worthwhile to use the theory applied to substances consisting of more than one kind of atom. The method is given in a paper by Warren, Krutter and Morningstar.⁶ What one obtains from such an analysis is a weighted distribution of the atoms surrounding any atom in the scattering substance, the weighting factor being practically the effective number of scattering electrons in each atom. The result is

$$\sum 4\pi r^2 K_m \rho_m(r) = 4\pi r^2 \rho_0 \sum Z_m + \frac{2r}{\pi} \int_0^\infty s i(s) \sin ks ds, \quad (1)$$

where

\sum indicates summation over a molecule
 $\rho_m(r)$ = density of atoms of type m about a given atom
 ρ_0 = mean electron density of scattering matter
 Z_m = atomic number of atom of type m
 $K_m = (f_m/f_e)$ average

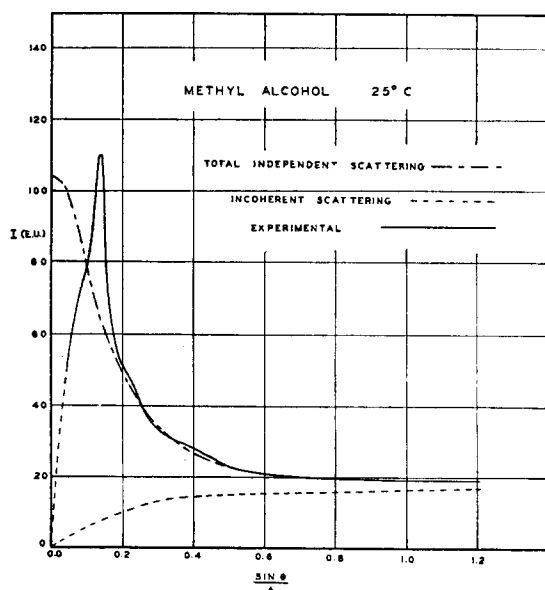


FIG. 1a.

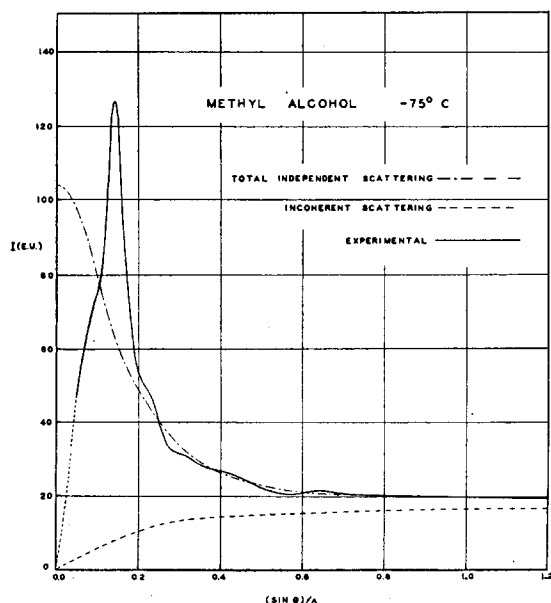


FIG. 1b.

⁵ S. Katzoff, J. Chem. Phys. 2, 841 (1934).

⁶ B. E. Warren, H. M. Krutter and O. Morningstar, J. Am. Ceramic Soc. 19, 202 (1936).

$$f_m = \text{scattering factor of atom of type } m$$

$$f_e = (\sum f_m) / (\sum Z_m) = \text{average } f \text{ per electron}$$

$$s = (4\pi \sin \theta) / \lambda; \quad 2\theta = \text{angle of scattering}$$

$$i(s) = (I_e - \sum f_m^2) / f_e^2$$

$$I_e = \text{coherent scattering per molecule in electron units.}$$

The integral in Eq. (1) is evaluated by a harmonic analyzer from a graph of the function $s i(s)$. The resulting weighted atom distribution curve is shown in Fig. 2a. The first peak corresponds to the intramolecular distance C—O and does not interest us here. The outstanding feature of Zachariasen's picture of liquid methyl alcohol is the existence of hydroxyl bonding between neighboring molecules. This would mean a more or less definite distance of about 2.7 Å between adjacent oxygen atoms. It is true that the curve in Fig. 2a does not drop to zero between 2 Å and 3 Å but there is no definite peak. Further, a dip, but not to zero, is typical of all liquid distribution curves.⁷ It would be much more convincing evidence of the essential reality of Zachariasen's model if a definite peak could be found at the approximate oxygen-oxygen distance for hydroxyl bonding. As Zachariasen has pointed out,¹ the strength of such bonds should depend on the temperature. At high temperatures the thermal energy of the molecules is sufficient to break up or prevent the formation of bonds. Obviously, a temperature should be considered as "high" if it is near the boiling point of the liquid and as "low" if far removed from that point. Methyl alcohol boils at about 65°C and freezes at about -98°C. Hence 25°C should be considered as a rather high temperature. The availability of a constant and convenient low temperature of about -80°C in the form of solid CO₂ immediately suggests itself. Accordingly the camera and circulating system were thermally insulated so as to permit the circulation of the alcohol at dry ice temperature. A mixture of dry ice and alcohol completely surrounded a reservoir of methyl alcohol just at the point where it flowed into the camera. Since the rate of flow was small it was not difficult to keep the flowing stream at practically dry ice temperature, roughly -75°C. A second series of pictures was taken at this temperature. Five diffraction rings were visible on the films

⁷ E.g., L. P. Tarasov and B. E. Warren, J. Chem. Phys. 4, 236 (1936).

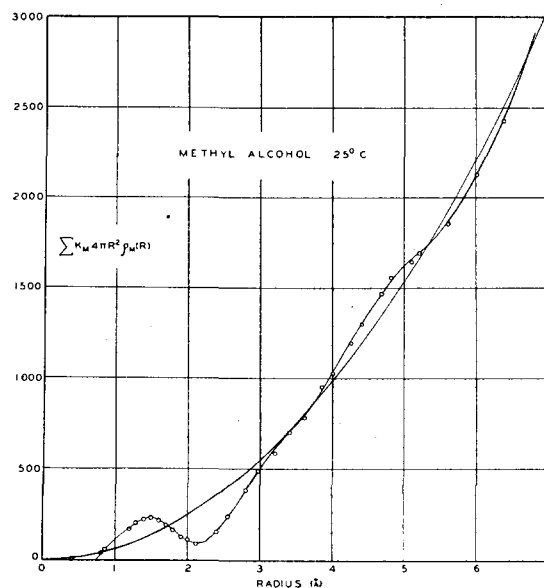


FIG. 2a.

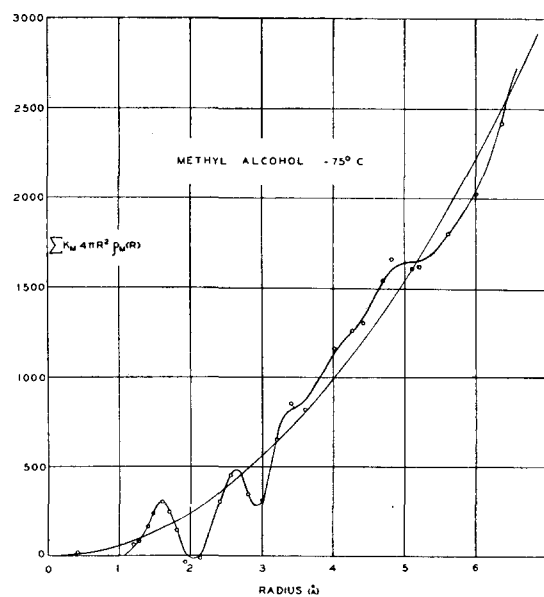


FIG. 2b.

whereas at 25°C it was difficult to distinguish a third one. The resulting intensity curve is shown in Fig. 1b. Upon analysis this lead to the distribution curve shown in Fig. 2b. The well-defined peak at about 2.7 Å gives immediate and convincing evidence for the existence of hydroxyl bonds.

The area under a peak measures the number of pairs of atoms a given distance apart, each weighted by its effective number of electrons.

In a molecule such as CH_3OH it is difficult to know how many electrons to assign to the carbon and how many to the oxygen and so one cannot say with certainty just what the area under a peak should be. There are eighteen electrons to be assigned to the molecule; this gives a definite (undoubtedly too large) upper limit to the area under the peak corresponding to $\text{C}-\text{O}$ of $2 \times 9^2 = 162$. The observed area is about 130. If we assign approximately 9 scattering electrons to the oxygen atom then from the measured area under the peak at 2.7\AA we may calculate the number of oxygen neighbors at this distance: $\text{Area} = n \times 9^2$. It is hard to know just how much to include in the area under this peak but in any case it is of the order of 200 units. Thus $n \approx 2$ in agreement with Zachariasen's picture. The positions of the other peaks are

practically the same as Zachariasen obtained from Stewart and Morrow's data and accordingly agree completely with his interpretation. It is felt that the peak in the distribution curve at 2.7\AA together with its disappearance at high temperatures gives very strong evidence for the truth of Zachariasen's picture of the molecular arrangement in liquid methyl alcohol.

It was planned to carry out a similar analysis on a whole series of the normal alcohols and some work has been completed on ethyl alcohol. Due to unavoidable delay and also to the fact that diffraction patterns from the higher alcohols are not nearly so straightforward of interpretation it is thought worthwhile to record the present results. The author is indebted to Professor B. E. Warren for his encouragement and interest throughout the work.

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The Isotope Effect in the Vibration Spectrum of CCl_4

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The fine structure in certain of the Raman lines of CCl_4 observed by Langseth and interpreted by him as being due to a lack of symmetry in the four carbon valencies has been shown to be accountable for as a purely isotopic effect. Rosenthal's general theory of the isotope effect in molecules of this type has been applied to the case of CCl_4 in an attempt to differentiate between two types of potential function which have been proposed for this molecule. The fine structure patterns predicted on the different theories have been worked out. Unfortunately the existing experimental data are not sufficiently good to allow a decision to be made as to which is the better function.

IN 1931 A. Langseth¹ reported that the Raman lines of carbon tetrachloride possessed a fine structure which he concluded was due to the different varieties of the compound arising from the presence of the two chlorine isotopes. Thus the five isotopic compounds CCl^{35}_4 , $\text{CCl}^{35}_3\text{Cl}^{37}$, $\text{CCl}^{35}_2\text{Cl}^{37}_2$, $\text{CCl}^{35}\text{Cl}^{37}_3$, CCl^{37}_4 should be present in the following relative percentages 31.6, 42.2, 21.1, 4.7 and 0.4. The proportion of $\text{CCl}^{35}\text{Cl}^{37}_3$ and CCl^{37}_4 being so small it may be taken that the Raman lines from those varieties of tetrachloride will be too weak to be observed; the remaining three varieties should each have their

own Raman spectrum differing slightly from one another and so giving rise to an apparent fine structure. The theory of the effect was worked out on very elementary lines by Langseth who found that although he could explain the fine structure in one of the Raman frequencies he could not account for the observed structure in the case of the two other frequencies in which it was observed. It occurred to us that the theory of this effect can be treated much more accurately now since the general equations have been developed by Rosenthal.² However in order to make numerical predictions it is necessary to

¹ Langseth, *Zeits. f. Physik* **72**, 350 (1931).

² Rosenthal, *Phys. Rev.* **45**, 538 and **46**, 730 (1934).