

The Liquid "Structure" of Methyl Alcohol

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and so sharpen the threshold. Although the steepness of the curves can be accounted for by the magnification of the intensity axis due to the high sensitivity of the counter, the same would apply to the temperature tail and its absence is somewhat remarkable.

SUMMARY

(1) A photoelectric counter has been used for measuring quantitatively the changes in the work function of gold due to adsorbed layers. The high sensitivity of the counter permits an accurate determination of the threshold with monochromatic light from a continuous ultraviolet spectrum of moderate intensity.

(2) The work functions of strongly oxidized and strongly reduced gold differ by 1.58 volts. The oxidation proceeds over two definite steps, with respective increases of 0.35 volt and 0.70 volt in the work function.

(3) The adsorption of iodine vapor on gold at room temperature is reversible and the resulting increase $\sim \Delta$ in the work function varies continuously with the iodine pressure according to a Langmuir isotherm. The value of $\Delta\phi$ at saturation is 0.2 volt.

(4) The adsorption of ethyl alcohol on gold gives rise to a double threshold consisting of (a) the original threshold of gold and (b) a new threshold corresponding to a decrease of 0.49 volt in the work function, this value being independent of the alcohol pressure. The intensity of the emission at the new threshold increases with increasing pressure. This suggests that the alcohol is condensed in the form of two-dimensional liquid islands, the area covered by these islands increasing with pressure.

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The Liquid "Structure" of Methyl Alcohol

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Fourier integral analyses of the x-ray diffraction patterns of liquid nonyl and methyl alcohol are made. From these the radial distribution of atoms around any one atom is obtained. On the basis of the radial distribution curves, conclusions are drawn concerning the molecular configuration in the liquid. For nonyl alcohol this analysis confirms the results of Warren. In the case of methyl alcohol the

analysis gives strong indication of hydrogen binding (dipole binding) between oxygen atoms of neighboring molecules. The short "life" of a given intermolecular bond in the liquid is emphasized. It is pointed out that the application of the ordinary Bragg equation to the peaks in the diffraction pattern of a liquid has no justification.

INTRODUCTION

RECENTLY B. E. Warren¹ published a paper dealing with x-ray diffraction in long chain liquids. He postulated a reasonable "structure" model of these liquids and showed that the diffraction curve calculated on the basis of the model was in agreement with the experimental curves measured by G. W. Stewart and collaborators. Warren considered the length of the chains to be practically unlimited, thereby

neglecting the effect which the presence of the end groups of the molecules have on the scattering curve. (It should be mentioned, however, that he gives an interesting explanation of the so-called "inner" peak in the diffraction curve in terms of the length of the molecule.) This effect becomes increasingly important as the number of carbon atoms in the chain decreases. It is therefore not surprising that the diffraction curve calculated by Warren shows little resemblance to the experimental curve of say methyl alcohol.

¹ B. E. Warren, *Phys. Rev.* **44**, 969 (1933).

It is well known that the alcohols show tendency to glass formation. In order to explain this glass forming tendency on the basis of the general picture of the vitreous state,² it was necessary to require the existence of definite bonds between neighboring molecules such that the formation of practically unlimited groups without symmetry and periodicity might be possible. It was to be expected that such definite bonds would exist to some extent even in the liquid state. For obvious chemical reasons this type of intermolecular bond would have to be between hydroxyl groups. Naturally such a binding will affect the radial atom distribution and thus the x-ray diffraction pattern. In the long chain alcohols this effect would be almost completely masked because the carbon-carbon distances predominate. In order to get definite information about possible intermolecular bonds,

an analysis of the experimental scattering curve of methyl alcohol was undertaken. For the sake of comparison an analysis was made of nonyl alcohol. In both cases the experimental data of Stewart and Morrow³ were used.

ANALYSIS OF THE X-RAY DIFFRACTION CURVES

The application of Fourier integral analysis to x-ray diffraction patterns of liquids is due to Zernicke and Prins⁴ and Debye and Menke.⁵ (Recently Warren and Gingrich⁶ have used the same method for powder patterns of crystalline substances.)

If the liquid contains only one kind of atom, and if $p_{(r)}$ is the continuous radial distribution around any one atom,* the intensity, $I_{(s)}$, of the unmodified part of the scattered radiation is given by:

$$I_{(s)} = \frac{e^4 I_0}{m^2 c^4 R^2} \frac{1 + \cos^2 2\theta}{2} f_{(s)}^2 N \left[1 + \int \frac{p_{(r)} \sin sr}{sr} dr \right]. \quad (1)$$

Here $s = 4\pi \sin \theta / \lambda$, $f_{(s)}$ is the scattering power and N is the total number of irradiated atoms in the sample. The integration is over the irradiated part of the sample. The radial function $p_{(r)}$ may be replaced by $4\pi r^2 \rho_0 + q_{(r)}$, where ρ_0 is the average density of the sample in atoms per unit volume. The function $q_{(r)}$ thus represents excess (or deficit) of actual radial distribution as compared to the average. Eq. (1) may then be written:

$$I_{(s)} = K \frac{1 + \cos^2 2\theta}{2} f_{(s)}^2 N \left[\int 4\pi r^2 \rho_0 \frac{\sin sr}{sr} dr + 1 + \int \frac{q_{(r)} \sin sr}{sr} dr \right] \quad (1')$$

where K is an abbreviation for $e^4 I_0 / m^2 c^4 R^2$. For all practical experimental set-ups the first integral will be zero unless $s=0$, in which case it is equal to N . Remembering that

$$I_{(s)} = K \frac{1 + \cos^2 2\theta}{2} N^2 f_{(s)}^2$$

one finds:

$$I_{(s)} = K \frac{1 + \cos^2 2\theta}{2} N f_{(s)}^2 \left[1 + \int_0^\infty \frac{q_{(r)} \sin sr}{sr} dr \right]. \quad (2)$$

Solving for $q_{(r)}$ by the Fourier integral theorem:

$$q_{(r)} = \frac{2r}{\pi} \int_0^\infty s \left[\frac{I_{(s)'} }{K(\frac{1}{2} + \cos^2 2\theta/2) N f_{(s)}^2} - 1 \right] ds, \quad (3)$$

² W. H. Zachariasen, J. Am. Chem. Soc. **54**, 3841 (1932).

where $I_{(s)}'$ is the unmodified scattering curve apart from the direct beam ($I_{(s)'} = I_{(s)}$). The observed intensity curve is readily corrected for modified radiation and Eq. (3) put upon an absolute basis through a simple procedure described by Warren and Gingrich (reference 6). The $q_{(r)}$ curves for methyl and nonyl alcohol are shown in Fig. 1. The scattering of the groups CH₃, CH₂ and OH was considered equivalent to

³ Stewart and Morrow, Phys. Rev. **30**, 232 (1927).

⁴ Zernike and Prins, Zeits. f. Physik **41**, 184 (1927).

⁵ Debye and Menke, *Ergebnisse der Techn. Röntgenkunde* **II**.

⁶ Warren and Gingrich, Phys. Rev. **46**, 368 (1934); Warren, J. Chem. Phys. **2**, 551 (1934).

* If all the atoms are not structurally equivalent, $p_{(r)}$ will represent a weighted average of the individual density functions.

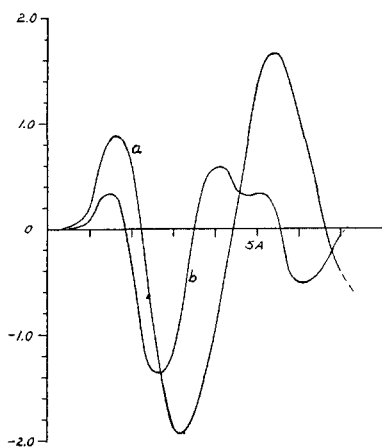


FIG. 1. The $q(r)$ -curves of nonyl alcohol (curve *a*) and of methyl alcohol (curve *b*) are shown.

that of oxygen atoms, so that the two liquids to this approximation consist of only one kind of scattering centers. The total radial atom distribution is obtained by adding $4\pi\rho_0r^2$ to the q_r -curve. The density, ρ_0 , of the two substances is 0.030 atom per \AA^3 for methyl alcohol and 0.0348 atom per \AA^3 for nonyl alcohol.

DISCUSSION OF THE RADIAL DISTRIBUTION CURVES

A. Nonyl alcohol

If we compare the $q(r)$ curve for nonyl alcohol with the corresponding curve constructed by Warren from his structure model (Fig. 2 of Warren's article), the striking agreement is apparent. Indeed, our result represents a most conclusive proof of the correctness of Warren's picture of the structure in the long chain alcohols.

TABLE I. Number of atoms between spherical shells.

r	From $q(r)$ curve	According to Warren's model
0-1A	0.2	0
1-2A	1.8	2 at 1.54A
2-3A	2.0	2 at 2.5A

The comparison of Table I serves to emphasize the quantitative agreement.

The peak in the q_r curve at about 1.6A corresponds to the shortest C-C distance in any

one chain (1.54A).^{*} The peak at 5.4A on the other hand corresponds to the shortest mean distance between carbon atoms of neighboring chains.

B. Methyl alcohol

To our approximation, methyl alcohol, $\text{CH}_3\text{-OH}$, should show only one intra-molecular distance, which would approximately correspond to the C-O distance. According to Pauling's⁷ radii the C-O distance is 1.43A. The peak in the $q(r)$ curve at about 1.5A is due to this distance. The quantitative agreement is quite satisfactory. Evaluation of the integral

$$\int_{r_1}^{r_2} [4\pi\rho_0r^2 + q(r)]dr$$

gives 0.1 atom in the range $0 \leq r \leq 1\text{\AA}$ and 1.1 atoms in the range $1\text{\AA} \leq r \leq 2\text{\AA}$.

If the molecules were held together by the usual van der Waals forces all interatomic distances between molecules would be fairly large. Thus we would expect the number of atoms between $r=2\text{\AA}$ and $r=3\text{\AA}$ to be approximately zero. The $q(r)$ curve, it is true, goes down to a minimum at about 3A; but the number of atoms between 2 and 3A comes out 1.3. Now the closest distance between methyl groups of different molecules is of the order of 4.0A.⁸ For chemical reasons it is hard to imagine any binding with resulting small distances between methyl and hydroxyl groups. We are therefore forced to the conclusion that every hydroxyl group is linked to the hydroxyl groups of two neighboring molecules at a distance of roughly $2\frac{1}{2}\text{\AA}$. Our analysis thus strongly indicates the presence of hydrogen bonds between oxygen atoms of neighboring molecules, similar to the hydrogen bonds between neighboring radicals in H_3BO_3 , KH_2PO_4 , and NaHCO_3 .⁹ Every hydrogen atom is thus linked to two oxygen atoms; undoubtedly it is linked more strongly to one of the oxygen atoms than to the other, so it

* It should be noted that the peak at 1.6A is somewhat influenced by the fact that the observed scattering curve breaks off at $s=3.7$.

⁷ L. Pauling, Proc. Nat. Acad. Sci. **18**, 293 (1932).

⁸ A. Müller, Proc. Roy. Soc. A **120**, 437 (1928).

⁹ W. H. Zachariasen, Zeits. f. Krist. **88**, 150 (1934); J. West, Zeits. f. Krist. **74**, 306 (1930); W. H. Zachariasen, J. Chem. Phys. **1**, 634 (1933).

still would be justifiable to talk about hydroxyl groups. Naturally if we wish to characterize the nature of these hydrogen bonds, we should employ the term dipole binding.

It must be emphasized that we do not believe that any one of these intermolecular hydrogen bonds persists in the liquid for an indefinite time. We expect rather that a given bond persists for a limited length of time (the duration being a function of temperature), that the bond then is broken and a new bond formed with another molecule. In other words, if we pick out a molecule at random, the probability of finding at a given instant hydrogen bonds between this molecule and two neighboring ones is appreciable; but there is no certainty. For general reasons this probability will decrease with rising temperature in the liquid.

The hydrogen binding between neighboring molecules is shown schematically in Fig. 2. Because of this binding the molecule under consideration can have no other immediate neighbor molecules in the right-hand solid angle of approximately 2π (see Fig. 2). The neighboring

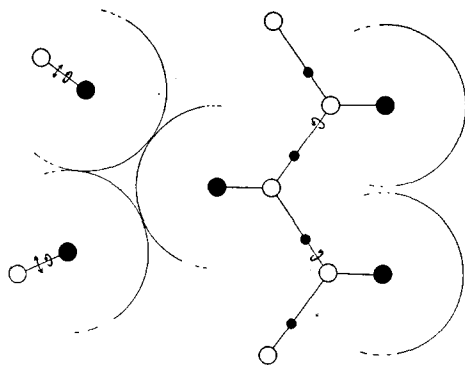


FIG. 2. A schematic picture of the molecular configuration in methyl alcohol is given. Carbon atoms are represented by large filled circles, oxygen atoms by large open circles and hydrogen atoms of the hydroxyl groups by small filled circles. The effective radius of the methyl group is indicated by the half circles around the carbon atoms. Only two of the six neighbor molecules in the left-hand part of the diagram are shown. The angle between the two hydrogen bonds is taken to be 110° , and the closest oxygen to oxygen distance is assumed to be 2.6\AA . The closest carbon to oxygen distance is 1.4\AA .

molecules within the solid angle of 2π to the left must point their methyl ends towards the molecule considered. Treating the methyl groups as approximately spherical there would be roughly six neighboring molecules in the space to the left. This would produce a peak in the $q(r)$ curve at a value of r corresponding to the methyl-methyl distance. Obviously the peak at about 4.1\AA has this origin. This value compares favorably with the methyl-methyl distance of 4.0\AA found by Müller in the *n*-hydro-carbons. The distance from the oxygen atom of the molecule considered to the same six methyl groups would lie between 4.5 and 5.6\AA , with an average of about 5.1\AA . The peak in the $q(r)$ curve for this value of r is thus accounted for.

Naturally we have to expect that also these neighbor molecules are constantly changing. Because of the weakness of the bonds between the methyl groups the time any one molecule will spend as neighbor of a given molecule must be extremely short, and the state of affairs may perhaps best be pictured as a reflection of the molecules when approaching the potential hill around the molecule considered. Hence it is impossible to talk about the existence of atomic planes, only the probability of interatomic distances can have significance, and this is indeed sufficient to account for the existence of x-ray diffraction in liquids.

It is well known that many experimenters have tried to gain information about the liquid state by a straightforward application of the ordinary Bragg equation to the peaks in the diffraction pattern. The “spacings” obtained in this manner naturally have no significance, except insofar as they may be re-interpreted in terms of interatomic distances by means of the extreme values of the function:

$$\sin sr/sr = \sin [2\pi r/d]/2\pi r/d.$$

The significance of the results of this investigation for the glass forming tendency of the alcohols will be taken up for discussion in a future article dealing with organic glasses in general.