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X-ray Studies on Liquids: the Inner Peak for Alcohols and Acids

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All of the straight chain aliphatic compounds, in the liquid state, give an X-ray diffraction pattern with a major peak at s[1] = 0.23 and with minor peaks at $s = 0.45$–0.50 and at $s = 0.80$. The diffraction pattern of paraffins shows no peak at smaller angle than the main peak but both alcohols and acids have an inner peak at small s-values.[2] The peaks at $s = 0.23$, 0.45–0.50 and 0.80 have been satisfactorily interpreted[3] as related to interatomic distances within the liquid. The major peak is due to interference between carbon atoms on neighboring molecules which tend to lie parallel to one another at distances of closest approach. The peak at $s = 0.45$–0.50 is due to second neighbors, at 2.5 Å., within a molecule, and the peak at 0.80 is due to the nearest neighbor, at 1.5 Å., in the molecule. No quantitative explanation has been given for the inner peak except for methyl alcohol,[4] but it is apparent that this peak is in some manner connected with the length of the molecule since the peak shifts to smaller angles as the number of carbon atoms in the molecule increases.

Fourier Analysis of Inner Peak

The most satisfactory interpretations of the X-ray diffraction from liquids have been made by Fourier analysis, using the Zernike and Prins equation[5] which is stated conveniently in the form

$$q(r) = \frac{2r}{\pi} \int_0^\infty k(E - 1) \sin kr \, dk \tag{I}$$

where $q(r)$ is the number of atoms at radial distance r in excess of the average (the average number of atoms at distance r is $4\pi r^2 \rho$ when ρ is the density in atoms per Å.^{3}), k is the function $4\pi \sin \theta/\lambda$, and E is the observed coherent scattering divided by the independent atomic scattering, f^2.

In order to apply this equation one needs an accurately determined scattering curve extending to large angles. Such a curve has not been reported for a long chain alcohol and it was necessary to determine one for a typical case. n-Hexyl alcohol was chosen since it is readily available, is of low volatility, and has a long hydrocarbon chain. The diffraction pattern was obtained photographically at room temperature, using a flowing jet of liquid as described by Katzoff.[6] Monochromatic copper Kα radiation was employed.

The diffraction curve, corrected for camera scattering, absorption, and polarization, is shown in Fig. 1, together with Katzoff's[6] data for n-heptane and those of Simard and Warren[7] for rubber. The curves were equalized at the $s = 0.80$ peak. The position of the major peak was found identical for heptane and hexyl alcohol, but the former gives much greater intensity because the measurement was made at low temperature, where a much greater degree of alignment prevails. The major peak for rubber is shifted to smaller angle, indicating greater interatomic distance. This is probably due to side chains in the molecule. The 0.45–0.50 peak is more pronounced for the alcohol than for the paraffin, probably because of the effect of the oxygen–oxygen distance in the alcohol. The chief point of difference in the alcohol curve is the inner peak, at $s = 0.07$. Although both the other curves are extrapolated in this region, the earlier experiments cited have shown that hydrocarbons give no inner peak.

The coherent scattering of the alcohol was determined (as shown in Fig. 1) by equating the observed scattering to the sum of the modified and coherent scattering of the single atoms at $s = 0.75$ and 0.95. No satisfactory fit of theoretical and experimental curves could be obtained by use of structure factors for either C° ($Z = 6$) or $C^{=}$ ($Z = 8$), but by using an average structure factor

$$f_{\text{alcohol}} = 6/7\, f_{\text{carbon}} + 1/7\, f_{\text{oxygen}}$$

based on the number of carbon and oxygen atoms in the molecule, we obtained the agreement shown in Fig. 1. From the corrected curves of Fig. 1 there was constructed a $k(E-1)$ curve which was

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(1) The symbol s is used for the function $2 \sin \theta/\lambda$, where θ is one-half the scattering angle and λ is the wave length.

(2) G. W. Stewart and R. Morrow, *Phys. Rev.*, **30**, 232 (1927); R. Morrow, *ibid.*, **31**, 10 (1928); G. W. Stewart, *ibid.*, **32**, 153 (1928).

(3) B. E. Warren, *ibid.*, **44**, 969 (1933); W. C. Pierce, *J. Chem. Phys.*, **3**, 252 (1935).

(4) W. H. Zachariasen, *ibid.*, **3**, 158 (1935).

(5) F. Zernike and J. A. Prins, *Z. Physik*, **41**, 184 (1927).

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

(7) G. L. Simard and B. E. Warren, THIS JOURNAL, **58**, 507 (1936).

plotted against k. The integration of Eq. I was performed by use of a Coradi harmonic analyzer[8] as suggested by Warren and Gingrich.[9]

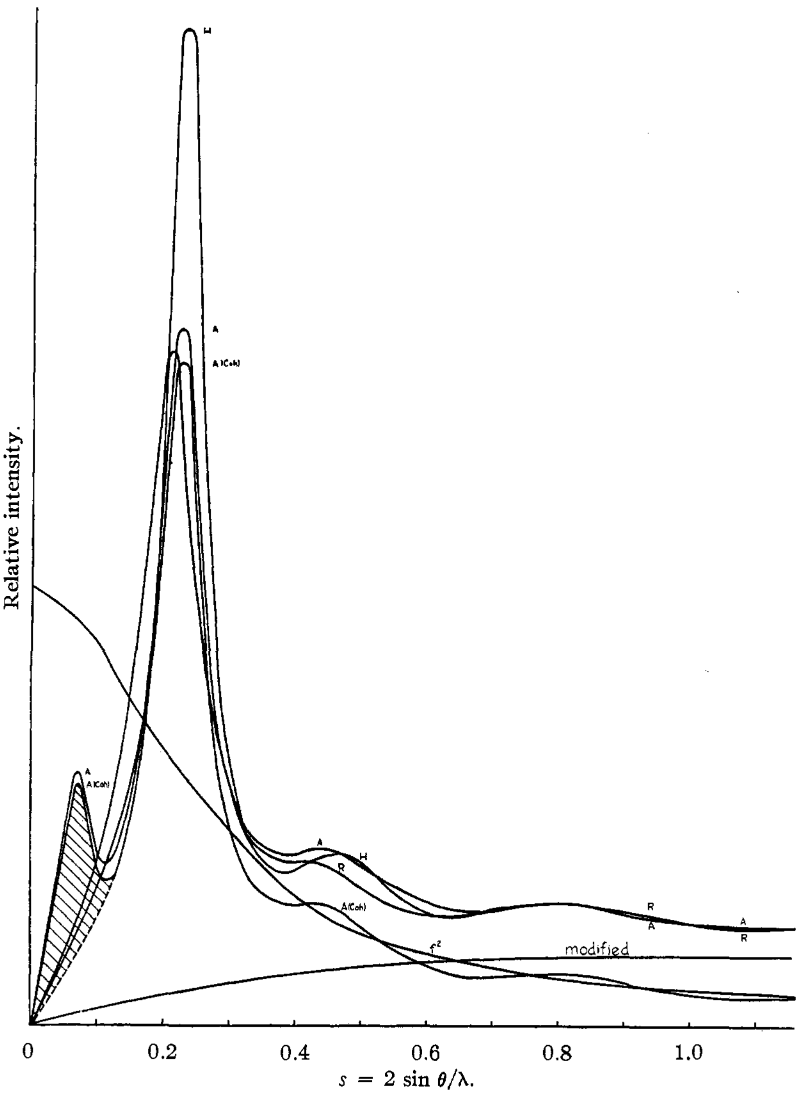

Fig. 1.—X-ray diffraction curves for n-hexyl alcohol (A), n-heptane (H) and rubber (R).

Radial atomic distribution curves for $q(r)$ and $4\pi r^2\rho + q(r)$ are given[10] in Fig. 2. Although the $q(r)$ curve was determined carefully up to r = 20 Å., there was found no large distance maximum which could correspond to the length of a single or double molecule. In fact, the $q(r)$ curve for the alcohol closely resembles those previously published for n-heptane and for rubber. This result was unexpected since we had thought that the radial distribution function would disclose a large interatomic distance that might cause the inner peak interference. Since no such distance was found it was necessary to resort to *difference* analysis to seek the distribution that gives rise to the inner peak. That is, an intensity curve was constructed for the difference in the diffraction of an alcohol and that of a paraffin. This difference curve was used for a Fourier analysis to give a distribution function $q'(r)$ which represents the number of atoms in an alcohol at radial distance r in excess of the number in a corresponding paraffin. Since

$$q(r)_{\text{alcohol}} = \frac{2r}{\pi}\int_0^\infty k(E_{\text{alcohol}} - 1) \sin kr \, dk$$

and

$$q(r)_{\text{paraffin}} = \frac{2r}{\pi}\int_0^\infty k(E_{\text{paraffin}} - 1) \sin kr \, dk$$

The excess scattering, $E_{\text{alcohol}} - E_{\text{paraffin}}$, is related to the excess number of atoms at distance r by the equation

$$q'(r) = q(r)_{\text{alcohol}} - q(r)_{\text{paraffin}} = \frac{2r}{\pi}\int_0^\infty k(E_{\text{alcohol}} - E_{\text{paraffin}}) \sin kr \, dk \qquad \text{(II)}$$

Analysis of the difference, represented by the shaded portion of Fig. 1, gave the $q'(r)$ curve of Fig. 2. This shows that the inner peak is due to an excess atomic density in the alcohol at r = 0 to 6.8 Å. and a deficit at r = 6.8 to 13.3 Å. At larger distances the $q'(r)$ curve is rapidly damped. Both the excess at small distance and the deficit at larger distance are necessary for producing the inner diffraction peak.[11]

The accuracy of the $q'(r)$ analysis was tested further by constructing hypothetical scattering

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[8] Available through the courtesy of Prof. Henry Schultz, Department of Economics, University of Chicago.

[9] B. E. Warren and N. S. Gingrich, *Phys. Rev.*, **46**, 368 (1934).

[10] The curve for $4\pi r^2\rho + q(r)$ gives the total number of atoms at distance $r \cdot \rho$ = 0.0341 atoms per cu. Å. for n-hexyl alcohol, density 0.82 (hydrogen atoms are neglected).

[11] Warren[3] explained the inner peak on the basis of an excess density at the COH group and a deficit at the end gap between molecules. This explanation fails to account for lack of an inner peak in an ester, which has two oxygen atoms attached to a carbon near the center of the chain (see below).

curves for alcohol and paraffin with the inner peak greatly exaggerated so that differences were magnified. Fourier analysis of the two curves gave $q(r)$ curves whose difference was identical with the $q'(r)$ curve constructed by application of Eq. II to the difference in inner peak intensity of hypothetical alcohol and paraffin. Finally, the procedure was reversed and scattering curves were constructed from $q(r)$ curves of alcohol and paraffin, using the equation

$$I_k = f^2\left(1 + \frac{1}{k}\int_0^\infty \frac{q(r)}{r}\sin kr\, dr\right)$$

The two scattering curves were reproduced accurately by this analysis.

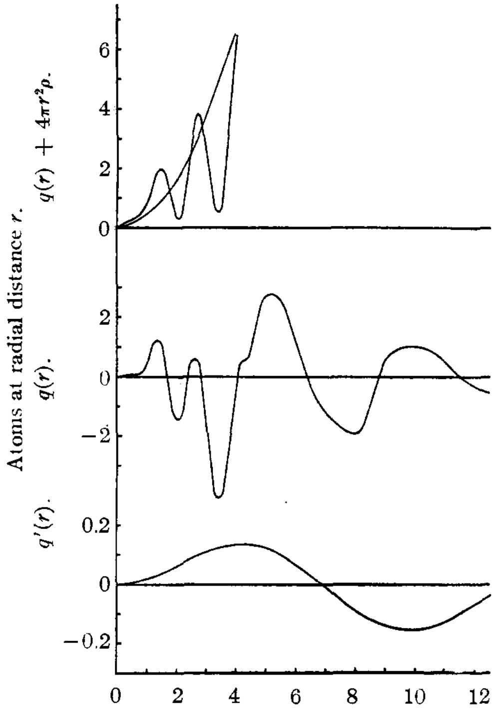

Fig. 2.—Atomic distribution for *n*-hexyl alcohol: upper curve, total number of atoms; center curve, $q(r)$; lower curve, $q'(r)$, enlarged scale.

Molecular Arrangement in Liquid Alcohols and Acids

Several lines of evidence must be considered in postulating a structure for the liquid alcohols and acids.

1. **Arrangement of Neighboring Chains.**—The main peak shows that the side by side arrangement of neighboring chains for alcohols and acids is like that of paraffins, as described by Warren.[3]

2. **Radial Distribution.**—An acceptable structure for alcohols and acids must differ from that of paraffins, esters, etc., in such a manner as to give the excess radial distribution shown in the $q'(r)$ curve of Fig. 2.

3. **Association.**—Both alcohol and acid molecules are associated by hydrogen bridges (or bonds) between COH groups.[12] Cryoscopic measurements on dilute solutions in non-polar solvents and Eötvös constants for pure liquids indicate that acids associate to form dimers whereas alcohols associate to an indefinite extent.

The atomic distribution which causes the inner peak is due to associated structures, not merely to the presence of oxygen atoms at the center of a molecule. This was proved by a determination of the diffraction pattern for ethyl propionate. The inner portions of the curve resemble that for *n*-heptane; there is no indication of an inner peak such as that found for *n*-hexyl alcohol.

4. **Molecular Volume.**—The molecular volumes of the lower liquid paraffins, together with the corresponding alcohols and acids, are shown in Fig. 3. The alcohols and acids of given number of carbon atoms, beyond the first two, have nearly identical volumes while the corresponding paraffins have a greater volume in each case. This difference is, since the side by side arrangement of chains is the same in all cases, due to a difference in the end gap for associated and non-associated molecules. The length of a doubly associated molecule is less than the length of two similar paraffin molecules. The molecular volume of an ester is practically identical with that of the paraffin of the same number of carbon atoms.

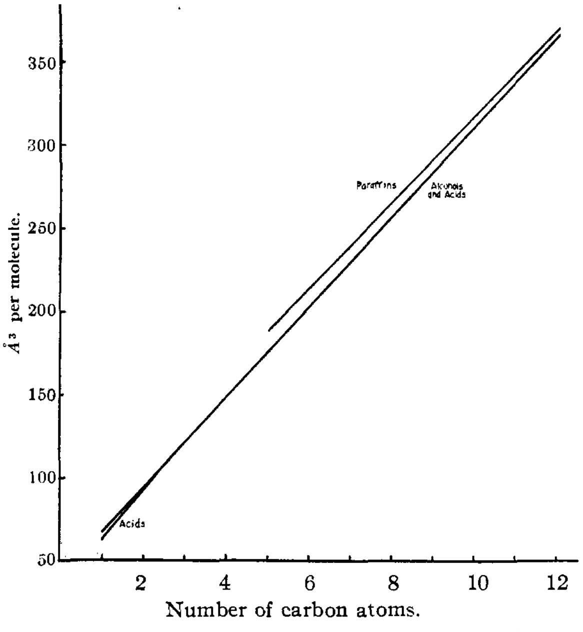

Fig. 3.—Molecular volumes of normal paraffins, alcohols and acids.

The increment in volume is about 26.2 cu. Å. per CH_2 group. If we assume the increment in length to be 1.25 Å. per carbon atom, as found for many crystalline substances, the length of a paraffin molecule of n carbon atoms may be obtained from the equation

$$L = 1.25\,(n - 1) + 3.85\ \text{Å}.$$

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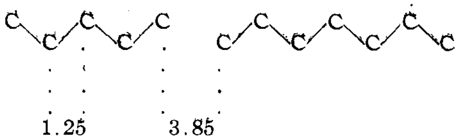
[12] M. L. Huggins, *J. Org. Chem.* 1, 407 (1937); E. N. Lassettre, *Chem. Rev.*, **20**, 259 (1937).

where the constant, 3.85 Å. represents the end gap between terminal CH$_3$ groups, as shown below



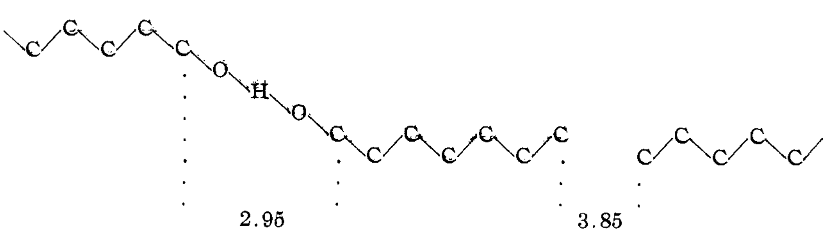
A similar computation, based on molecular volume, gives for the length of a single acid or alcohol molecule

$$L = 1.25\,(n - 1) + 3.40$$

If the assumption is made that the molecules are associated with the polar ends together, and that the end gap at the non-polar ends is the same as for paraffins, the length of associated molecules is given by

$$L = 2 \times 1.25\,(n - 1) + 2.95 + 3.85 \text{ Å.}$$

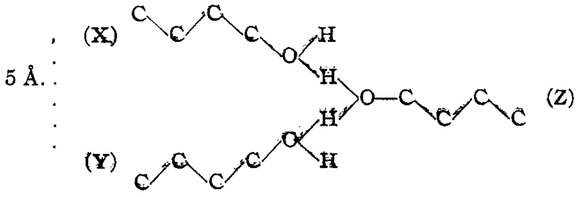
where 2.95 Å. is the carbon–carbon distance at the associated group as shown below



Although there is no direct evidence for the assumption that the molecules lie extended in zigzag chains (rather than curling into the various configurations possible with free rotation about the C–C bond), the linearity of the molecular volume data and the agreement of the computed end gaps with those found in crystals support the view that this is probably a correct picture.

Mechanical models were used to seek possible liquid structures in harmony with the various conditions listed above. In using these models we assumed, C–C distances of 1.54 Å., with tetrahedral angles; C–O distances of 1.4 Å., with tetrahedral angle for singly bound oxygen; O–H–O distances of 2.6–2.8 Å. with oxygen valence angles of 120° and with hydrogen valence angles of 180°.

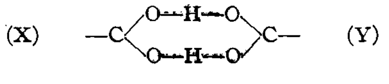
The most probable structure found for associated alcohol molecules was (projected onto the plane of the paper)



In this structure molecules (X) and (Y) lie in the plane of the paper while molecule (Z) lies parallel to this plane but at a distance of 1.5–2 Å. above it. An associated group may include more than the three molecules shown, but cannot be of infinite extent because, as the number of chains is increased, the valence angles must be distorted to permit additional chains to lie parallel to the three shown.

According to the structure given above, the oxygen atoms are concentrated near a plane which passes through the center of the associated molecule at right angles to the chain axis. This concentration of atoms near the center of a cluster of molecules is apparently the source of the distribution which causes the inner peak, since ethyl propionate does not give the inner peak. The atomic distribution in an associated cluster of molecules will differ from that of a paraffin just in the manner indicated by the $q'(r)$ curve. Each carbon atom in the alcohol has the same carbon neighbors as a corresponding carbon atom in a paraffin, but it has in addition oxygen neighbors concentrated at the center of the cluster. Moreover, the oxygen atoms have carbon neighbors at distances extending to the length of a single chain on both sides of the center. Thus, over a distance equal to one-half the diameter of the cluster there is an average excess atomic density, followed by a deficit at the end gap. The positive portion of the $q'(r)$ curve cannot give accurately the length of the single chain because (1) experimentally the shape of the $q'(r)$ curve depends upon an extrapolation of the scattering curve from the main peak to zero angle, and (2) the $q'(r)$ curve is an average radial density function not a linear function. For the same reasons the negative portion of the $q'(r)$ curve does not accurately measure the length of the end gap beyond the molecular cluster.

Dimer acid molecules may be represented by a structure whose projection is



In this structure the chains (X) and (Y) do not lie in the same plane, but in parallel planes and the O–H–O bridges run diagonally between the two planes. In order to form the closed ring in a plane, according to the Pauling and Brockway[13]

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[13] L. Pauling and L. O. Brockway, *Proc. Nat. Acad. Sci.*, **20**, 336 (1934).

model for formic acid molecules in the vapor state, it is necessary to assume a C–C distance of 3.9 Å. Although there are no *a priori* reasons for ruling out such a structure, the identity of molecular volumes of acids and alcohols, together with the other deductions which have been made on the basis of molecular volume, lead us to favor the non-planar structure.

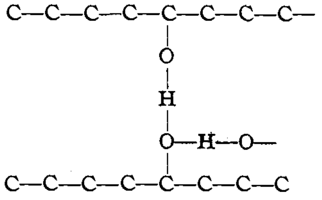
The dimer structure alone does not account for the inner peak for acids since the associated molecule does not differ greatly in atomic distribution from an ester. It is probable, therefore, that in the liquid acid there is a tendency for neighboring molecules to form a cluster with the carboxyl groups of adjacent molecules lying directly above one another as shown

$$C-C-C-(COOH)_2-C-C-C$$
$$C-C-C-(COOH)_2-C-C-C$$

The distribution in such a cluster will be similar to, but not identical with, the distribution in an alcohol cluster. Experimentally, the inner peaks of an acid and the corresponding alcohol do not coincide in position, but in most cases the alcohol inner peak occurs at slightly smaller angle. If the acid dimers do cluster in the manner suggested, the binding between neighboring dimers is slight. The Eötvös constants for alcohols and acids indicate more complex association for the alcohol. Likewise viscosity data suggest that the alcohol molecule is more complex, since at the same temperature an alcohol has considerably higher viscosity than an acid of equal carbon content.

There is no implication of crystalline structure in the liquid arrangements suggested. The orientation of neighboring molecules represents a condition at the distance of closest approach. Due to thermal agitation there is, on the average, marked disarray, even of closest neighbors, and at a distance of several molecular diameters there is no reason to assume any fixed orientation. The concentration of oxygen atoms near a plane perpendicular to the chain axis is also only a local distribution. It is not necessary to assume large molecular clusters or large oxygen-rich planes in order to explain the X-ray scattering from liquids.

The present theory provides a simple explanation for the apparently anomalous X-ray diffraction observed by Stewart for the four isomeric straight chain octyl alcohols.[14] All four of these octanols-1, -2, -3, -4, give a main peak similar to that of *n*-hexyl alcohol (Fig. 1). Octanol-1 gives an inner peak, at $s = 0.062$, and octanol-4 gives a very pronounced inner peak at $s = 0.086$. Octanols-2 and -3 give no sharp inner peak, but the diffraction curve shows inflection points at small angles. The inner peak of -1 is like that of *n*-hexyl alcohol and is similarly explained. The peak for -4 is due to a side by side association of parallel chains so as to form an oxygen-rich plane at the center of the molecule



It can be shown, with a space model, that other parallel chains may be joined to the unoccupied hydrogen so as to give a high degree of association. Since the oxygen atoms are concentrated near the center of the cluster in this model, we may expect a pronounced $q'(r)$ distribution with excess over a distance roughly equal to one-half the length of the single chain—thus the inner peak is large and is found at larger angle than for the normal alcohol. For -2 and -3 such an association will lead to an unsymmetrical molecular cluster and no sharp $q'(r)$ peak is to be expected since the oxygen-rich plane will lie near one end of the parallel chains.

Summary

It has been shown, by Fourier analysis, that the inner X-ray diffraction peak found for aliphatic liquid acids and alcohols is due to an atomic distribution not present in other liquids, such as the paraffins and esters. This distribution is explained on the basis of molecular clusters which are due to association by means of hydrogen bridge formation so that there is in a cluster a plane rich in oxygen atoms. This plane lies at right angles to the hydrocarbon chains. Neighboring chains are roughly parallel to one another, just as in the paraffins. The theory is applied for the interpretation of the X-ray diffraction found by Stewart for the isomeric octyl alcohols, some of which give inner peaks while others do not.

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(14) G. W. Stewart, *Phys. Rev.*, **35**, 736 (1930).