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X-RAY DIFFRACTION IN LIQUIDS: A COMPARISON OF CERTAIN PRIMARY NORMAL ALCOHOLS AND THEIR ISOMERS

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Abstract

This x-ray diffraction study of certain isomers of the liquid primary n-alcohols confirms, in general, present conceptions concerning the alteration in shape of the chain molecule with the attachment of branches, and it emphasizes the importance of the molecular space array in liquids, or the cybotactic state, and an investigation of it by x-ray diffraction. One isomer of n-butyl, five of n-amyl, one of n-hexyl, and two of n-heptyl alcohol were tested. It is found that the attachment of CH_3 as a side branch alters the "diameter" by 0.6A and of OH by 0.4A (Ångstrom units, 10^{-8} cm.) The attachment of CH_3 and of OH to the same atom in the chain increases the diameter by only 0.65A. The diameter is in a sense a mean value, but in the case of the di-n-propyl carbinol there is a better resolution and the side attachment of OH increases the diameter in one direction by 0.45A and in the other not at all. The existence is shown of associated polar groups giving two molecules in a continuous chain for each longitudinal spacing. When the OH group is not attached to the last or next to last atom in the chain this association disappears and there is but one molecule for each longitudinal spacing. This is in agreement with other experiments. In the one case carefully tested, triethyl carbinol, the first, third and fifth orders of the side spacing peak are apparently present. The assumption of a molecular space array seems the only one consistent with the facts.

THE view expressed in an earlier article by Stewart and Morrow[1] is that there is a molecular arrangement in liquids which is similar to but not the same as the crystalline state, and that this arrangement is of significance in the action of liquids. So important seems the conception in a consideration of liquid phenomena that the name "cybotaxis" has been given to this condition in matter. A study of the molecular arrangement, or the cybotactic state, by means of x-rays has at least three purposes in view: to learn to what extent diffraction measurements can serve to analyze the molecular space array, to give evidence concerning molecular structure either confirmatory or new and, chiefly, to verify the existence of the cybotactic state and give it wider recognition as a factor in the behavior of liquids.

That a clearer conception of phenomena in liquids is desirable is indicated by the incompleteness of our understanding of viscosity, solubility, osmosis and molecular activity, this list of four being cited as illustrative and not as comprehensive. With the advance in our knowledge of the crystalline

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[1] Stewart and Morrow, Phys. Rev. **30**, p. 232 (1927).

state has come new contributions to theoretical physics, as in atomic heats, to our meager knowledge of molecular forces and to current views concerning molecular structure. While the cybotactic state is not as easy to visualize as is a crystal yet its effects and hence its existence are quite definite. From a comparison of heats of evaporation of solids and liquids, it is easy to see that the molecular forces acting in the two states are of the same order of importance. Similar conclusions are obtained from compressibilities and densities. In a crystal the molecules or atoms, as the case may be, are held in relatively stable positions, but in a liquid this stability disappears. However, the forces acting in the latter case would doubtless compel an approximation to a molecular arrangement at any point and the more elongated the molecule, as in a chain, the better the approximation. It is generally agreed that in a crystal the forces cause the material to simulate a continuous acoustic medium and that random motion of the individual molecule does not occur. It is reasonable to accept the same view with reference to a liquid. This approximate arrangement in a liquid, lacking stability, would vary continuously in detail from point to point. But at some places the variation is more rapid than at others. This distributed irregularity implies mobility and slippage. In fact, this picture opens the way for an explanation of variations in viscosity with composition. In many other respects this view, which seems to be in harmony with all the facts, must be important.

A recent contribution by Shearer,[2] referring particularly to the thin films of Langmuir, Adam and others, suggests that any attempt at molecular orientation in a liquid is essentially an attempt at crystallization and should produce a more or less perfect replica of some aspect of the orientation found in a crystal. Our view gives a uniqueness as well as definiteness to the molecular arrangement in the liquid state. Both the crystalline state and cybotaxis are results of molecular forces. Both represent physical states worthy of study.

In addition to the contributions mentioned in the earlier paper,[1] several have recently appeared which are pertinent to the general subject of liquid x-ray diffraction. Sogani[3] has studied 22 liquids belonging to the aliphatic and aromatic groups. He has shown that the formula of Ehrenfest,[4] applicable to the scattering from a diatomic molecule in a gas, in general does not give the mean molecular distance, that the theory of Raman and Ramanathan,[5] particularly concerning the effect of compressibility, is in harmony with anticipation in the appropriate portion of the experiments, and that the x-ray diffraction patterns with different molecular structures are sufficiently varied to cause the method of study of molecular structure to appear promising. Raman and Sogani[6] have studied the molecular structure by the

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[2] Shearer, Farady Soc. Trans. **22**, 465 (1926).

[3] Sogani, Indian Journal of Physics I, p. 237 (1927). In a later paper which has just come to our attention, Ind. Jl. of Physics Vol. II p. 97 (1927), Sogani takes much the same viewpoint of this and our earlier paper.

[4] See Keesom and Smedt, Proc. Roy. Soc., Amsterdam **25**, 118 (1922) and **26**, 112 (1923).

[5] Raman and Ramanathan, Proc. Ind. Assoc. Culv. Sci. **8**, p. 127 (1923).

[6] Raman and Sogani, Nature **119**, p. 601 (1927).

sharpness of rings in the case of hexane (diffuse) and cyclohexane (sharp). Clark, Aborn, Brugmann and Davidson[7] have shown that information of practical bearing can be obtained by the diffraction patterns of rubber and its substitutes, and that with china wood oil when prepared in a stated manner and dried, there are evident changes in spacing indicating combination with solvent molecules and polymerization Diffraction photographs of numerous liquids have recently been made by Katz.[8] He used one isomer of n-propyl alcohol, two of n-butyl alcohol and two of n-amyl alcohol. In each case he gets the diminution of the radius of the diffraction ring for the isomer. Only in cases of the isomers of n-amyl alcohol can comparison be made with the results of this paper. The increases in the spacing when computed by Bragg's formula for isoamyl and tertiary amyl alcohol are in close agreement with those here presented. But Katz found only one ring, and in his discussion he used the Ehrenfest formula which should not, because of the very nature of its assumptions, be applied to liquids. Herzog and Jancke[9] have made a comparison of diffraction rings in the liquid and solid state, but none of the compounds corresponds to any one in this paper.

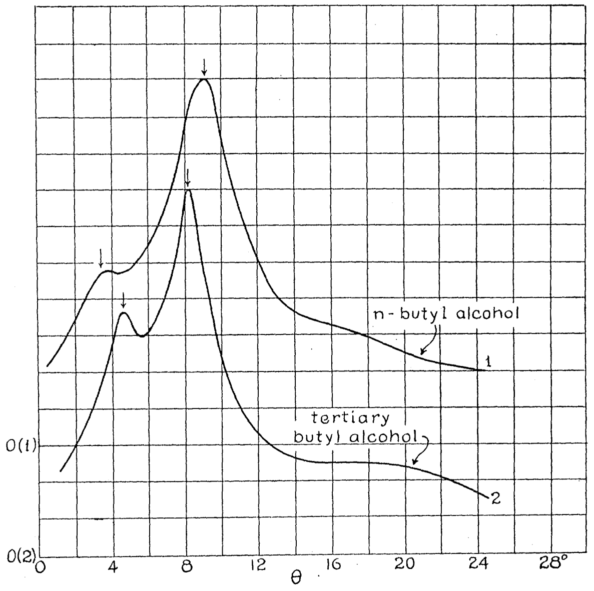

Fig. 1. Relative diffraction intensity with n-butyl alcohol and an isomer.

The present contribution is a continuation of the study[1] of the primary alcohols. The apparatus is essentially the same as previously described. The x-ray diffraction ionization curves were obtained with isomers of primary n-alcohols. The liquids were isoamyl alcohol, secondary amyl alcohol,

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[7] Clark, Aborn, Brugmann and Davidson, Proc. Nat. Acad. of Sci. **13**, p. 549 (1927).

[8] Katz, Zeitschr. für Physik **45**, p. 97 (1927).

[9] Herzog and Jancke, Zeitschr. für Physik **45**, p. 194 (1927).

tertiary amyl diethyl carbinol (special sample), methyl n-butyl carbinol, tertiary butyl alcohol, secondary butyl carbinol, triethyl carbinol. All these but one were obtained from the laboratory of the Eastman Kodak Company. Triethyl carbinol was obtained from R. E. Marker, Yonkers, New York.

RESULTS

The diffraction curves of the isomers, and of the primary normal alcohols previously reported,[1] are given in Figs. 1, 2 and 3. Each curve is a mean of three or more complete sets of observations. As in the case of the primary normal alcohols the isomers have two equivalent planar spacings. The computed values of these, using the wave-length 0.712A for the Mo $K\alpha$ radiation, are shown in Table I. They represent the observations with an accuracy less than 0.5A. Here also are given the boiling point ranges indicating the purity of these alcohols, the structure of the molecules as accepted by chemists, and the width of the principal peaks in Ångstroms. In the structural formulas the H atoms attached to the carbons are not indicated.

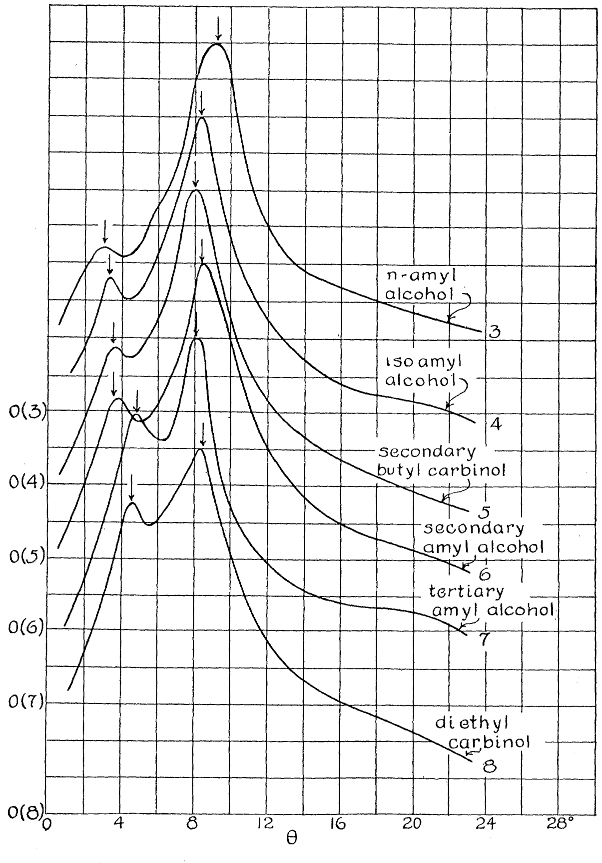

Fig. 2. Relative diffraction intensity with primary n-amyl alcohol and isomers.

The earlier interpretation[1] of the two peaks was that one spacing was caused by the length of the chain molecule and the other by its diameter. The evidence for this was the fact that the former altered linearly with increase of carbon content in the chain and the latter, although it increased slightly with increased carbon content, approached a constant value as the length of the molecule was increased. This interpretation of the spacings represented by the peaks is here regarded as justifiable and the conclusions, as before, are in harmony with this opinion. It is not claimed that the spacing normal to the chain has only one value. In one case in this report, two such spacings are found. But, inasmuch as there is, in general, no separation of such values, the spacing represented by the high peak is called the "diameter" of the molecule.

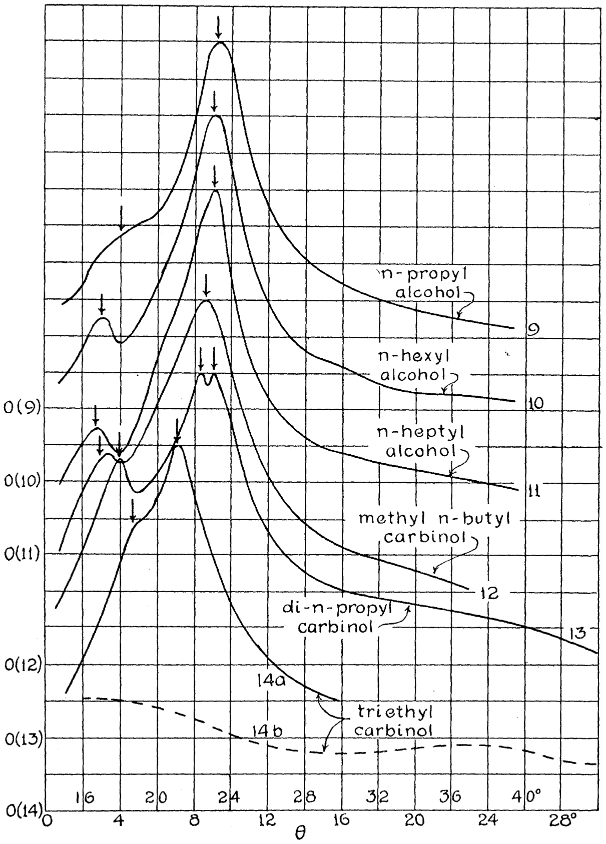

Fig. 3. Relative diffraction intensity with primary n-hexyl alcohol and isomer, primary n-heptyl alcohol and two isomers, and primary n-propyl alcohol.

In the discussion of the results it is well to remember that, as is indicated by the range of boiling point temperatures, the samples were not pure. A slight impurity might easily alter the peaks sufficiently to make *exact* values of the spacings untrustworthy. But in the previous work on primary normal alcohols the boiling point ranges were as large as with these isomers and yet the results for the spacings were capable of being expressed by smooth curves without serious deviations therefrom. The present discussion assumes no greater purity for these isomers and hence the conclusions are probably well within appropriate bounds. This, and the fact that the conclusions are consistent with present chemical beliefs, give confidence in the approximate correctness of the results and of the interpretations.

TABLE I

Computed values of the two equivalent planar spacings.

Name	Boiling Point °C given by maker	Two "Planar" Dist. $\times 10^8$ cm.	Structure	Peak Width Diffraction angle
1. Primary n-butyl	116°–118°	4.4; 11.1	C-C-C-C-OH	3.3°
2. Tertiary butyl	14°–15° (m. p.)	4.95; 8.7	C | C-C-OH | C	3.0°
3. Primary n-amyl	136°–139°	4.4; 12.6	C-C-C-C-C-OH	3.2°
4. Isoamyl	130°–132°	4.9; 12.2	C-C-C-C-OH | C	3.6°
5. Secondary butyl carbinol	126°–128°	5.1; 11.3	C-C-C-C-OH | C	2.8°
6. Secondary amyl	116°–118°	4.8; 11.3	C-C-C-C-C | OH	4.0°
7. Tertiary amyl	100°–102°	5.05; 8.5	OH | C-C-C-C | C	1.9°
8. Diethyl carbinol	115°	4.85; 8.9	C-C-C-C-C | OH	3.3°
9. Primary n-propyl	96°–98°	4.4; 9.5	C-C-C-OH	3.4°
10. Primary n-hexyl	155°–157°	4.4; 14.2	C-C-C-C-C-C-OH	3.4°
11. Primary n-heptyl	172°–176°	4.4; 15.7	C-C-C-C-C-C-C-OH	3.1°
12. Methyl n-butyl carbinol	136°–139°	4.75; 14.9	OH | C-C-C-C-C-C	3.9°
13. Di-n-propyl carbinol	154°–156°	4.85 and 4.5; 10.5	OH | C-C-C-C-C-C-C	4.0°
14. Triethyl carbinol	138°–139°	5.75; 8.9	C | C | C-C-C-OH | C | C	4.3°

DIAMETER OF THE MOLECULES

Adopting, as explained, the high peak, or the first "planar" spacing in Table I, as determining the diameter of the chain molecule, the following conclusions may be drawn:

1. The attachment of CH_3 at the side of the chain increases the diameter by 0.6A (Cf. 1 or 3 and 5, 0.7A; 1 or 3 and 4, 0.5A. The numbers refer to the samples in Table I.)

2. The attachment of OH at the side of the chain increases the diameter by 0.4A. (Cf. 3 and 6, 0.4A; 3 and 8, 0.45A; 10 and 12, 0.35A.) This change is noticeably less than in the case of CH_3 just cited.

3. The attachment of OH and CH_3 at the sides and to the same carbon atom increases the diameter by 0.65A. (Cf. 1 or 3 and 7.) This change is practically the same as with the side attachment of CH_3 only.

4. The attachment of three chains of C_2H_5 to the same carbon atom, increases the diameter by 1.35A (cf. 9 and 14) when compared with one such chain. This is suggestive as to an arrangement but it is not the purpose of the paper to enter upon this detail at present. In the case of sample 2 there might be a similar molecular structure.

5. The two adjacent peaks of case 13, di-n-propyl carbinol, indicate that the two planar distances normal to the chain are now separately determinable. One of them, presumably increased by the side attachment of OH, is distinctly greater (i.e., by 0.45A) than in the case of primary n-alcohol but the other diameter is approximately unchanged. This is the only liquid thus far examined in which the components of this peak are resolvable. The increase in diameter of the longer normal spacing by OH, 0.45A, is (cf. 11 and 13) in fair agreement with the preceding second conclusion.

If the above is quantitatively reliable it shows that the increase in diameter by CH_3 and OH are not additive. A similar statement may be made with reference to the fourth conclusion, or it may be said that the straight lines representing three pairs of CH_3 are not in the same plane. In this discussion it must be borne in mind that, on account of the lack of sharpness of the peak, what is called the diameter of the molecule should be regarded as a mean value.

LENGTH OF THE MOLECULES

A consideration of the length of the molecules is not so fruitful for the angle made by the length of the molecule with the effective planes is not known. Computation from Table I shows that if the volume occupied by the molecule is assumed to be the square of the shorter spacing multiplied by the longer one, the density of every sample but one of the fourteen is smaller than the known densities which vary from 0.79 to .84. According to this assumption, the length of the molecule is equal to the larger spacing and is hence normal to the corresponding group of planes. If the density so computed is much less, there are presumably two molecules to a single spacing, and in order to account for the known density, there must be an inclination of the length to the normal to the planes. If the density is approximately correct, there may be only one. In cases 1, 2, 3, 4, 5, 6, 9, 10, 11, 12 and 14 the computed density is so much smaller that it is reasonable to suppose an association of two OH groups, making two molecules in a chain instead of one in each long spacing. Computation shows that these long double molecule chains could not be normal to the planes having the spacing discussed. In each of these eleven cases it is noticed that the OH group is either at the end of the chain or adjacent to it. However, 2 and 14 may not necessarily be regarded as having OH at the end of a chain. It is notable that in the case of 8 and of 13, the OH is symmetrically situated and presumably could not have this association. Here the density computed as stated, assuming one molecule in each spacing, is -14 percent and $+2$ percent in error. It is of interest that in case 13 where the computed density is so nearly the true one, there is increased accuracy of measurement, for there are two molecular diameters instead of one. With case 7, the OH, although adjacent to the end, may have its associative quality reduced by the presence of an additional CH_3. Here the density, assuming one molecule to a spacing, is -16 percent in error. We see that in these three cases the assumption of no association of the molecules of the nature referred to, is confirmed by the x-ray interpretation. A similar conclusion was reached by Saville and Shearer[10] with solid, aliphatic ketones. They found that methyl ketones, having the CO group near the end of the molecule, seemed to have the double molecule, whereas the ethyl, propyl, etc., ketones with the CO further removed from the end had single molecules only. It is evident that although this discussion does not presume to discuss the exact arrangement of molecules and is only very general, yet the agreement between the x-ray interpretation and the accepted view of the molecular structure is striking. This fact adds confidence in the application of Braggs' law to the cybotactic state and consequently in the view point of this contribution.

WIDTH OF PEAKS

The width of a peak is a measure of the sharpness of the resolution, provided it represents only one spacing. As already indicated, there may be two such spacings and the interpretation of the width of the peak may mean partly that. Furthermore, the chemicals are not of the highest degree of purity and this is an important consideration. Nevertheless, it is well to indicate that in all but one of the seven cases where the OH or CH_3 group was made a side branch, the width of the peak is increased thereby. In two cases where two side branches are attached to the same carbon atom, the width of the peak seems to be decreased.

ADDITIONAL PEAKS

In the case of triethyl carbinol, there is a very definite indication, as shown in Fig. 3, of peaks at about 20° and 37.5°. There are at least two interpretations as to corresponding spacings. The more probable one is that these peaks are the third and fifth orders of the 7.1° spacing. Assuming 7.1° to

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[10] Saville and Shearer, Chem. Soc. J. **127**, p. 591 (1925).

be correct the orders should appear at 21.4° and 36.1°, respectively. Inasmuch as triethyl carbinol is, according to the above, a branched molecule with CH_3 in branches but with two OH groups associated, the distribution of electrons might account for the absence of the peaks of even orders. For, as Shearer[11] has proved, with a concentration of electrons at the center of the molecule, the even orders would have relatively small intensity. The other interpretation would arise from a consideration of the additional peaks as of the first order. The corresponding spacings would be 2.05A and 1.11A. The separation of carbon atoms in diamond is 1.54A. But if the distances of separation be projected on a mean straight line, values of 2.0A for pairs and 1.26A for single atoms are found. These peaks may therefore be due to the separation of the carbon atoms in the molecule.

Current Theories

In the preceding paper,[1] attention was directed to theories of the liquid x-ray diffraction halo. The two most prominent ideas involved therein are (1) that peaks may be occasioned without the necessity of an arrangement of molecules, and (2) that the spacing corresponding to the peak depends upon the compressibility (Raman and Ramanathan). With reference to the first, it is granted that a peak in the diffraction ionization curve would occur with random orientation and the mean distance between molecules could easily be the effective spacing as computed by Bragg's law. But the experiments on primary normal alcohols[1] cannot be explained by random orientation of the molecules, for the chief peak remains practically constant in position with large changes in molecular lengths. The results demand a parallel arrangement of molecules. The admission of this conclusion brings one at once to the viewpoint of the authors, namely, that we are discussing an arrangement and not random orientations. There is no doubt but that our effective spacings are mean values, but this lack of exact homogeneity in the liquid does not destroy either the definiteness of the molecular arrangement (as judged by its effects) or the importance of its investigation. In regard to the effect of compressibility, it may be said that the theory is not applicable to long chain molecules, for here the molecular arrangement overshadows the considerations upon which the effect of compressibility is based.

The conclusions of this paper as set forth emphasize not only the desirability of a similar study with purer samples, but also the importance of the continued systematic study of liquids in general. The authors desire to acknowledge the assistance obtained through conferences with Professors L. C. Raiford and J. N. Pearce of the Department of Chemistry.

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[11] Shearer, Roy. Soc. Proc. **A108,** p. 655 (1925).