X-RAY DIFFRACTION IN LIQUIDS: PRIMARY NORMAL ALCOHOLS

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Abstract

Evidence for a molecular space array in liquid primary normal alcohols, methyl to lauryl.—The x-ray diffraction in liquids has long been known. The suggestion has been repeatedly made that the effect is caused by fragmentary crystals. The viewpoint here taken is that there is a molecular space array, not crystalline, which is named *cybotaxis*. Evidence of the cybotactic state in liquid primary normal alcohols, methyl to lauryl, is adduced. By Mo $K\alpha$ x-ray diffraction ionization curves, two significant distances are measured, the first linearly dependent upon the content of carbon atoms and the second practically independent of this change in molecular length. The latter is thus the distance of separation perpendicular to the chain, and is 4.6A with lauryl, decreasing slowly to 4.4A with butyl and then rapidly to 3.8A with methyl. The value 4.6A is in striking agreement with the work of Adam on surface films of saturated fatty acids. The increase of the first distance, linearly with carbon content, is in harmony with the work of Müller and Saville and others, in that the increase is about 1.3A per carbon atom, and leads to the conclusion that the diffraction is produced by planes containing the polar groups, which are not perpendicular to the direction of the parallel chain molecules. Comparison of peaks in the liquid and solid states show that the spacings are not the same and the phenomena is not caused by crystal fragments. The cybotactic state permits mobility, but not random motion and is peculiar to the substance. The distances computed are the most probable spacings. The molecules may be regarded as having the same orientation in a small group, too small to give optical anisotropy. The discussion does not, therefore, extend to liquid crystals but adheres to the more general condition. The conception of the cybotactic state is helpful in an understanding of solutions and other liquid phenomena. The theories of Raman and Ramanathan, Debye and Zernike and Prins are suggestive in that they indicate that a definite molecular space array is not necessary for the production of a single diffraction halo. But they in no sense negate the evidence here adduced for a cybotactic state.

I. Introduction

THE crystalline state demonstrates the complexity of the atomic forces concerning which we know but little. In the crystal there is evidently a stable space-array, the atoms or the molecules occupying lattice points and resisting deformation. But the laws underlying atomic forces can scarcely be regarded as discontinuous at the melting point. True, there is a discontinuity in position stability, but this does not require any discontinuity in the fundamental forces considered separately. As an illustration of the existence of a critical temperature, at which there is a discontinuity in stability, there may be cited the not unusual transformation from one crystal form to another. Such considerations make it difficult to accept the view, that at a certain temperature and pressure, a compound can pass from a definite space array of molecules or crystalline structure to a fluid with no semblance of space array and an entirely random motion of the molecules. In fact

other reports of experiments with x-ray diffraction in liquids have suggested the existence of a space array in liquids, but their authors have not believed the evidence of a definite space array to be convincing. Moreover, the explanations of the x-ray diffraction halo in liquids, made from other view points, have been not fully satisfactory.

The contribution of the present paper gives strong evidence for a molecular space array in the liquid primary normal alcohols, with carbon content of from one to eleven atoms. It interprets the space array observed not as caused by fragmentary crystals, but by a type of molecular arrangement wherein there is combined mobility of the component molecules and yet a recognizable space array. To this state is given the name "cybotaxis," which means "space-arrangement." The adjective is "cybotactic." A new word is necessary in order to distinguish this state from that called "crystalline."

II. The X-ray Diffraction Halo in Liquids

The diffraction halo in liquids, using the Laue spot method, was first reported by Debye and Scherrer.[1] Debierne[2] investigated the liquids mercury, methyl iodide, methylene iodide, benzene, and bromobenzene, and concluded that there need not be a simple crystalline arrangement of the atoms. Hewlett,[3] by an ionization method, found a diffraction maximum with benzene, mesitylene, and octane and suggested that these liquids have "something of a crystal structure." Keesom and Smedt[4] studied the phenomenon in liquid oxygen, argon, and nitrogen, and in carbon disulphide, benzene, water, ethyl alcohol, ethyl ether, and formic acid. They found a second ring measurable in the cases of oxygen, argon and nitrogen. Their opinion was that the effect is caused by neighboring molecules.

Wyckoff[5] experimented with liquids and liquid mixtures and concluded that the origin of the diffraction was within rather than between the molecules.

Eastman[6] compared the patterns obtained with crystalline and liquid benzene and showed a similarity.

Liquid crystals, so named because of their anisotropic optical properties, have been studied with x-rays. M. de Broglie and E. Friedel[7] have proposed that there exists for matter between the amorphous and crystalline states, two possible intermediate states of matter, "nematique" in which the molecules are distributed at random, but all have a common direction, and "smectique," in which the molecules have a common direction and are arranged in equidistant parallel layers. As will be later realized, the present contribution is not immediately concerned with optically anisotropic liquids.

[1] Debye and Scherrer, Nachr. Gesell. Wiss. Göttingen, p. 6 (1916).

[2] Debierne, Comptes rendus, **173**, p. 140 (1921).

[3] Hewlett, Phys. Rev. **20**, p. 688 (1922).

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

[5] Wyckoff, Am. Jour. Sci. **5**, p. 455 (1923).

[6] Eastman, J. Am. Chem. Soc. **46**, p. 917 (1924).

[7] de Broglie and Friedel, Comptes rendus, **176**, p. 738 (1923).

These consist of very long molecules, and represent an extreme case of space array in liquids. Hückel[8] shows that liquid crystals do give an x-ray pattern. But this report is concerned not with the case of molecular array sufficiently extensive to give optical anisotropy, but with a more general type of array where mobility is distinctly in evidence and the molecules do not have the same direction over a volume whose diameter is large compared with the wave-length of optical rays.

III. CURRENT THEORIES

The theories proposed in explanation of the x-ray diffraction halo in liquids may be regarded as successful in one respect. They have shown that the presence of a maximum does not require equidistant spacing of molecules.

Raman and Ramanathan[9] treat the fluid as a continuous substance subject to local changes in density determined by thermodynamical considerations. Their result gives a graph very much like the experimental curves of Hewlett.[3] The maximum intensity of diffraction occurs at an angle that is approximately determined by Bragg's law using the mean distance of separation of the molecules as a grating distance. This distance λ_0, lies between $0.8 \times \bar{n}^{1/3}$ and $1.0 \times \bar{n}^{1/3}$, where n is the number of molecules per $\overline{cm}^3$. Raman and Ramanathan also refer to Ehrenfest's formula quoted by Keesom and Smedt,[4] in which the interference is caused by two neighboring molecules, and to Brillouin's theory[10] based upon the quantum theory of specific heats. He shows that neither of these agree with experiment in the neighborhood of zero angle of scattering.

Debye[11] derives an approximate theory assuming that the effect is caused by neighboring molecules, and that each molecule scatters as a whole. He finds a maximum in the scattering curve which occurs at an angle defined by the quotient of the wave-length of the radiation and the diameter of the sphere assumed occupied by the molecule. He also considers the case of scattering wherein the molecule consists of two scattering centers. By this means he obtains a maximum and at larger angles, a series of maxima. Both of these theories give an angle of maximum intensity of diffraction that is of the observed order of magnitude.

Zernike and Prins[12] have just published a theory in which they consider the problem first as that of a one dimensional molecule acting as a point. Diffraction curves are computed which are like those observed in that they have a sharp maximum and very little intensity at small angles. In extending the theory to actual liquids, spherical symmetry is assumed, and the theory put in a form so that one can ascertain the effect of neighboring molecules on one another from the diffraction observations.

[8] Hückel, Phys. Zeits. **22**, p. 561 (1921).

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

[10] Brillouin, Ann. d. Physique, p. 88 (1922).

[11] Debye, Jour. of Math. Phy. **4**, p. 133 (1925), (published by the Massachusetts Institute of Technology) also translated for Phys. Zeits. **28**, p. 135 (1927).

[12] Zernike and Prins, Zeits. f. Physik. **41**, p. 184 (1927).

Debye's paper does not refer to the contributions of Raman and Ramanathan, and Zernike and Prins refer to neither of the other theories. Doubtless this is because the journals containing the first two reports were not widely distributed. The chief contribution of all three theories is not that they explain the phenomena herein described, but that they indicate strongly that a maximum in the diffraction intensity *may* occur without equidistant spacing. Other than this conclusion, none of the theories has any immediate bearing upon the discussion of our results. In fact, it appears from the experiments described in this article that, for the present, the need is for experimental data to guide any future theory which must include the operation of molecular forces on anisotropic molecules.

IV. EXPERIMENTAL PROCEDURE

The fluids were enclosed in very thin-walled closed cylindrical glass tubes, and when in use a tube was rotated with the axis of the cylinder coincident with the axis of the spectrometer. The x-rays from a molybdenum Coolidge tube passed successively through a slit set, the liquid mounted as described and into the ionization chamber attached directly to the second slit. The collimator and the ionization chamber slits each consisted of a Soller[13] slit set, 20 cm long, containing 8 slits each 0.079×1.6 cm in cross-section. The separating lead walls were each 0.0076 cm in thickness.

The total width of a slit set was 0.8 cm. Thus a relatively large area of the target could be utilized. Moreover, in order to obtain the optimum thickness[14] it was necessary to use cylindrical samples having diameters greater than the width of a single slit and usually of a slit set. These cylinders were rotated in order to eliminate any effect due to inequalities in the glass containers.

The ionization chamber of Allison and Clark[15] was modified by the substitution of quartz insulation for Pyrex. It was found that the insulation was entirely satisfactory and that when the chamber was once filled with methyl bromide, no serious change in content could be observed over the time of several months. The chamber was 30 cm in length. Whether or not the chamber gave relative intensity relations with the different wave-lengths, is not an important consideration in these experiments.

Observations were made in the usual manner by recording the electrometer needle velocity in scale divisions per second. The instrument was a Dolezalek pattern with a sensitivity of about 2500 divisions per volt. The corrections of observations were made as follows:

1. For the natural electrometer drift.

2. For the x-rays passing through the system without being diffracted, especially when the angle of diffraction becomes small. This correction was

[13] Soller, Phys. Rev. **24**, p. 159 (1924).

[14] I.e., thickness $=1/\mu$, where μ is the absorption coefficient, Hull, Phys. Rev. **10**, p. 661 (1917).

[15] Allison and Clark, J.O.S.A. **8**, p. 681 (1924), refers reader for diagram to Hudson J.O.S.A. **9**, p. 259 (1924).

of importance only for chamber settings of less than 2.5° from the direction of the incident rays. It was obtained by noting the ionization current in the neighborhood of zero angle in the absence of the diffracting sample, and then by correcting this value for the absorption of the sample which was found by observation of direct transmission. In order to secure these comparisons at such high intensities, a heavy lead plate with a narrow horizontal slit was placed in front of the ionization chamber Soller slit-set. It is to be observed that these corrections are chiefly for the x-rays penetrating the walls of the slit system. One could get within 0.5° of the zero setting and yet make satisfactory corrections.

3. The diffraction curve of one of the empty glass cylinders showed a maximum at a diffraction angle of about 11°, but the slope on either side was very gradual. In fact, the correction for the glass curve appeared unimportant and was omitted.

The Coolidge molybdenum x-ray tube was operated by a transformer. Inasmuch as the primary voltage was not sinusoidal the selections of the desirable value of primary effective voltage was determined by experiment, and no direct measurement of secondary voltage was made. A sheet of zirconium oxide, obtained from the General Electric Company, absorbed about two-thirds of the $K\alpha$ radiation but gave a satisfactory isolation of this doublet, $\lambda = 0.71 \times 10^{-8}$ cm. Its success is illustrated by the diffraction curve of a non-homogeneous crystal, frozen lauryl alcohol, shown in Fig. 4. Here the width of the $K\alpha$ doublet is about 24', in agreement with the geometry of the case.

The selection of the liquid samples was a very important matter. A space array that is not crystalline but has fluidity would surely not be easily identified. It would have a low resolving power, not only on account of the small size of a somewhat homogeneous group, but also because of the nature of the group itself. The prospect of definite results seemed to depend upon a comparison of diffraction curves obtained with molecules varying in size and shape in a systematic manner. The selection was therefore made from liquids having chain molecules, with dimensions increasing in but one direction. The primary normal alcohols were chosen because of their availability. The molecule is generally believed to consist of a chain of carbons, each laterally bonded to two hydrogen atoms, and the chain terminated at one end with H and at the other end with OH. Thus the increase in length can be made by the addition of CH_2. Our experiments are in accord with this description. In the tests this addition of CH_2 was made ten times, the samples covering all the normal alcohols from methyl, CH_3OH, to lauryl, $C_{11}H_{23}OH$. Nine of these were obtained from the laboratories of the Eastman Kodak Company. Decyl was supplied by Fritsche Bros. Inc. Ethyl was prepared by Mrs. Roger M. Morrow.

V. Experimental Results

Nature of radiation. That the zirconium screen isolated the $K\alpha$ doublet satisfactorily was proved by tests on a crystal powder. The unseparated

doublet was the only observed characteristic radiation, but the general radiation was confusing and had to be virtually, though not actually, eliminated. This was accomplished by the use of an appropriate voltage. Fig. 1 shows the change of an alcohol diffraction intensity curve with alteration of the voltage. The principal maxima are plotted to the same scale but with displaced ordinates. The curves are designated by the primary voltages on the transformer. It is apparent that the peaks at approximately 2°, 5° and 9°, are not caused by the same radiation, for the alteration of voltage seriously modifies the relative value and position of one of the three.
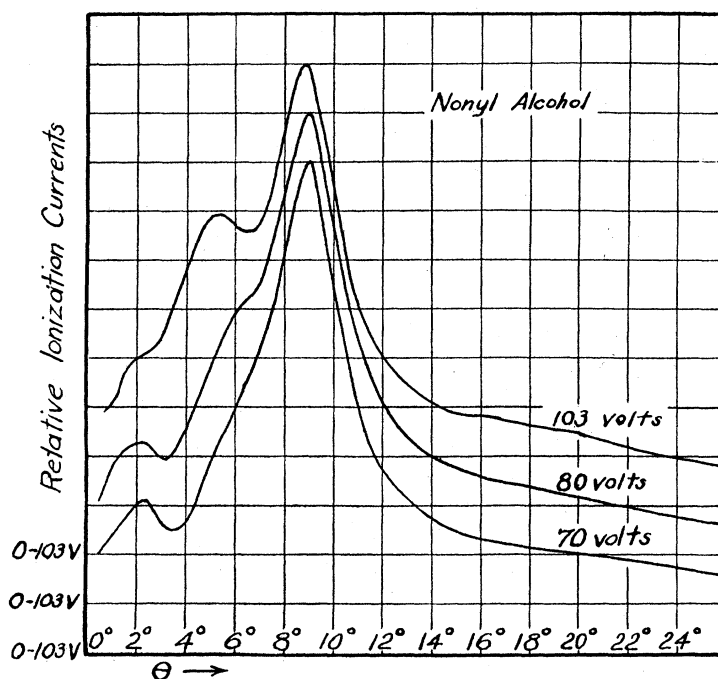

Fig. 1. Intensity-diffraction curve with variation in primary voltage.

This peak is thus identified as caused by the general radiation. Our knowledge of the commercial circuit alternating current was not sufficient to check the position of this peak. An approximate check (see Siegbahn's Spectroscopy of x-rays p. 208) indicates that the peak with 103 volts, r.m.s. primary, and 46.3 K.V. maximum secondary should be at about 0.39A. Assuming the peak 8.9° to be produced by the .71A radiation, the diffraction angle of 0.39A should be at 5°. The variation in absorption of the zirconium screen would, of course, shift the peak to smaller angles. The observed position of the central peak is in accord with the interpretation that it is caused by the general radiation.[16]

[16] A test of absorption was made by means of a 2 mm aluminum screen and it was found that the absorption of the 9° peak was 95 percent and the 5° peak was 50 percent. These values are consistent with the interpretation of the former as 0.71A and the latter of 0.44A.

Fig. 1 also shows that the same radiation, i.e., 0.71A, is responsible for the peaks at 2.2° and 8.9°. The important conclusions from Fig. 1 are (1) that 70 volts, effective value, on the primary partially avoids the confusion caused by general radiation, and (2) that two peaks are caused by the same radiation, 0.71A.
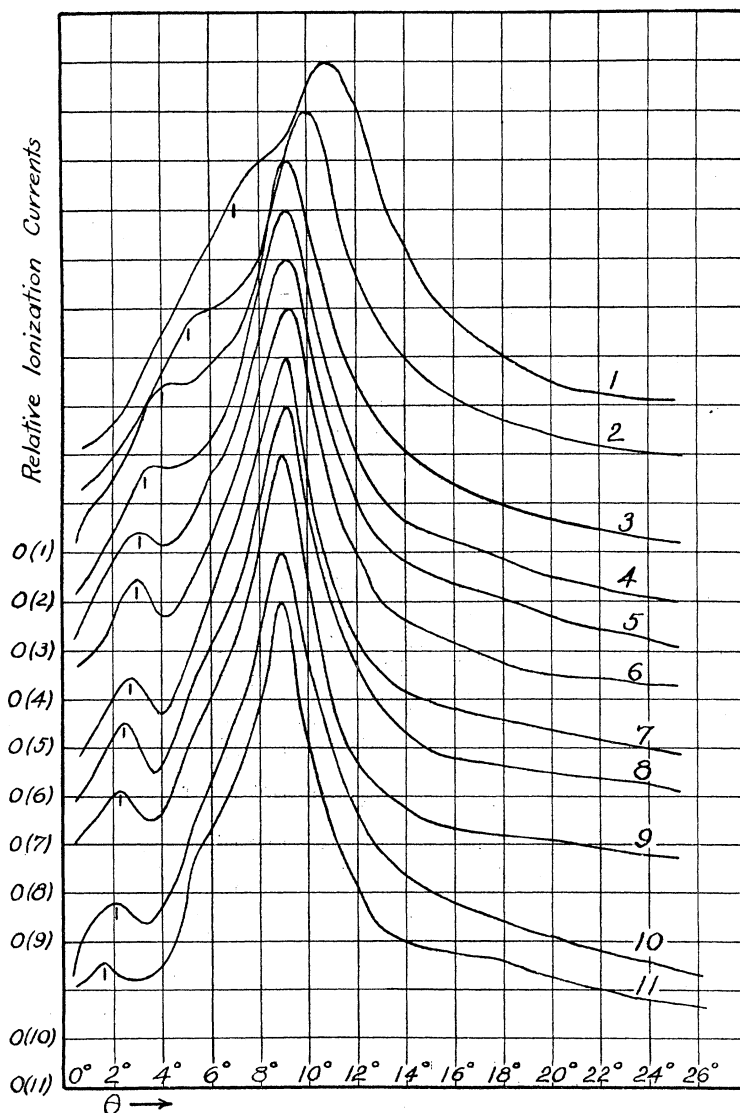

Fig. 2.   Intensity-diffraction curve with normal alcohols containing
from one to eleven carbon atoms.

Variation of diffraction with increasing content of CH₂. In Fig. 2 are shown the diffraction curves for the normal alcohols from methyl to lauryl, in-

clusive. In order to show all of them in one figure the ordinates are displaced as indicated by the zero ordinates shown on the left. The voltage on the primary was 70 effective volts. The curves are designated by numbers which indicate the content of carbon atoms in the molecule. Each curve is a mean of three. For some of the peaks more than three curves were averaged.

Computed "planar" distances. Fig. 3 shows the angular positions of the peaks and the corresponding planar distances computed by the formula, $0.71 = 2d \sin (\theta/2)$ where θ is the angle of diffraction.
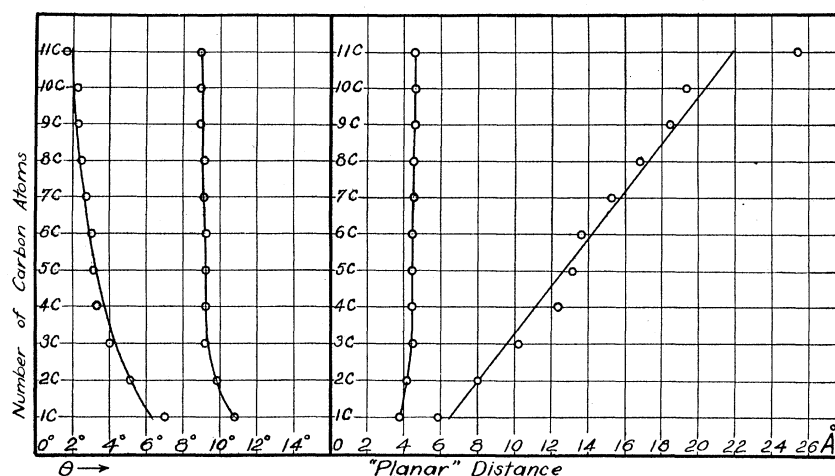

Fig. 3. Variation of diffraction peaks and "planar distances" with content of carbon atoms in the molecule.

Comparison of solid and liquid states. In order to shed light upon the physical condition in the liquid state, curves for lauryl alcohol, $C_{11}H_{23}(OH)$, shown in Fig. 4, were taken with the liquid and the solid. The liquid was at 21°C and the solid at practically its melting point 19°C.

VI. DISCUSSION OF RESULTS

Inter-planar distances. The term "inter-planar" is used not with the sense that there is a fixed orientation of molecules determined by planes, but merely as referring to inter-planar distances determined by Bragg's law. The experiments clearly show, as in Fig. 3, the variation of two such distances, d_1 and d_2, and that the cause of the large variation in d_2 is not the same as the cause of the small variation in d_1. The former is linear and the latter is not. Since the variation in d_2 is linear, about 1.54A for each CH_2 addition (see below) the accepted shape of the molecule as a "chain" leads to the conclusion that d_2 is determined by the length of the molecule. Since d_1 is not altered linearly, it must be caused by the separation of molecules measured perpendicularly to their lengths. Moreover d_1 would, on account of molecular symmetry, probably represent two distances, approximately alike. It appears from Fig. 3 that d_1 approaches a limiting value for further addi-

tions to the molecular length. Of course the curve should not be extrapolated, *but if the further additions of CH_2 merely lengthen the molecule, 4.6A may be accepted as the mean distance, or most probable distance between adjacent long chain molecules made up of CH_2.* That this agrees with other measurements, will later be mentioned.

Length and arrangement of molecules. The above shows that, while 4.6A may be interpreted as the distance of separation of the molecules, the other inter-planar distance may or may not be the length of the molecule. There are two reasons for believing that it is not. In the first place, the alcohol molecule is strongly polar, the active group being OH. It is probable that in any alignment of the molecules in the direction of molecular length, these polar groups would be together. In the second place, approximate computa-
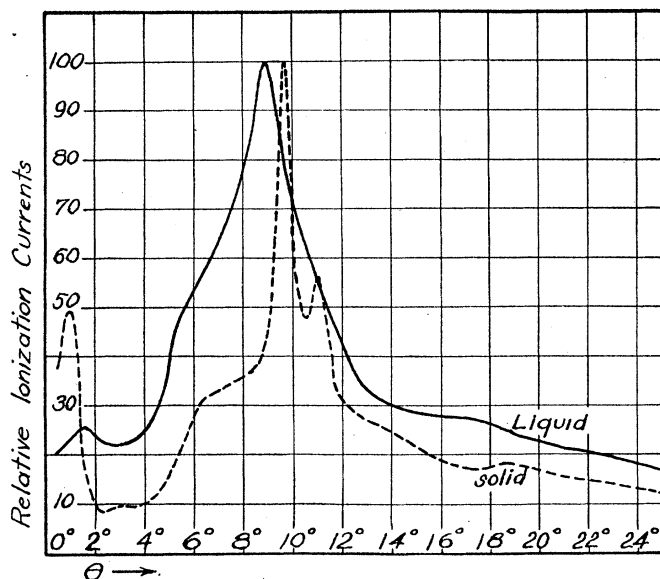

Fig. 4. Diffraction curves of solid and liquid lauryl alcohol.

tions of density from the above planar distances give evidence for this arrangement of molecules. Consider first that the distance d_2 is caused by the spacing occasioned by one molecule only and (as is assumed throughout) that in the plane perpendicular to this length, the molecules are arranged at the corners of squares. Then the density would be $\rho = 1/d_1^2 \times 1/d_2 \times$ (molecular weight) $\times$ (mass of H atom). Substituting respectively the values 4.6×10^{-8}, 20.4×10^{-8}, 158, and 1.66×10^{-24}, ρ becomes 0.60. But this density is much too small, the correct value being approximately 0.83. If d_2 be assumed caused by two molecules, as suggested in the preceding paragraph then the density 0.60 would be doubled. Assume the molecules to be aligned as above indicated, but let the polar groups occur in pairs along any line of molecules. If these pairs be now shifted so that they are in planes forming equal intercepts on three rectangular axes, one of which is in the

direction of the molecular lengths, then the distances from one pair to any of its neighbors in any of these planes is constant. Two neighboring pairs are not immediately adjacent, or at a distance d_1, but at a distance $2^{1/2} \times d_1$ from one another. With this arrangement the distance between two planes is $0.576 \times 2a$, where a is the length of a molecule. For decyl alcohol, for example, a is $10.2A/0.576$ or $17.6A$. If the density of decyl be now computed as above, it is 0.70. Of course by adjusting the planes at a different angle an arrangement can be found that will give the actual density, but if assumed as already stated the result is strikingly in accord with several other facts as will now be explained.

Adam[17] experimented with films of saturated fatty acids on the surface of water. His experiments were with carbon chains ranging from twelve to twenty-six carbons. These differ from the alcohol chains only in that the polar group at the head in the water is COOH instead of CH_2OH. It was found that with the films on water, the area occupied by one molecule, oriented perpendicularly to the surface, was 21.0×10^{-16} cm^2, and that this value was independent of the nature of the acid. If, however, he used a solution of HCl, $N/100$, the corresponding area was 25.0×10^{-16} cm. The interpretation at present accepted is that in the latter case the polar groups are adjacent, and in the former they are alternated in position vertically in such a manner that the polar groups are not side by side. *It is most interesting to note that the area, 21.0×10^{-16} cm^2 is precisely $(4.58 \times 10^{-8}$ cm$)^2$. Hence the surface film measurements agree with our determination of d_1 or 4.6×10^{-8}, and the relatively displaced positions of the polar groups occur in both cases.* This comparison may be said to give confirmatory evidence of the correctness of the interpretations given in the two widely different cases, the surface film and the liquid interior. This area of cross section of a CH_2 group is also confirmed by estimations made in other ways. It is thus with great confidence that the distance 4.6×10^{-8} cm is to be accepted as the planar distances between the molecules in the liquid.

Each CH_2 group adds to d_2 one-half of $1.54A$ or $0.77A$. This represents an increase in a of $0.77A/0.576$ or $1.33A$. This is the longitudinal separation of C atoms in the chain and is of the proper order of magnitude.

A comparison should also be made with the experiments of Müller and Saville[18] on long chain hydrocarbons in the solid state. There they found the addition per C atom to be 1.3×10^{-8} cm or approximately the same as in the liquids. This reference is only to one of several experiments in which this change in length with C atoms is of the same order. The correspondence between the solid and liquid experiments gives greater confidence in the interpretation of both.

Another interesting confirmatory point is the alteration of density of the alcohols. The formula for density is obtained by dividing the molecular weight by the volume occupied by a molecule, or the length of the molecule

[17] Adam, Proc. Roy. Soc. 99A, p. 336 (1921); 101A, p. 452, p. 456 (1922); 103A, p. 676, 687 (1923).

[18] Müller and Saville, Journal Chem. Soc. 127, p. 599 (1925).

times $d_1{}^2$. The length of the molecule is found from the above interpretation of arrangement to be 4.32A plus $n \times 1.33$A where n is the number of carbon atoms. Hence the entire formula for density will be $\rho = (18 + 14n) \times 1.66 \times 10^{-24} [(4.32 + 1.33n) \ d_1{}^2 \times 10^{-24}]^{-1}$. The values computed for eleven of the alcohols are compared in Table I with the known values of density. It is to be noted as a matter of interest that if the computed values are regarded as 20 percent in error, because of the inaccuracy of the approximate arrangement described, then the final computed values, with one exception, agree within less than 5 percent with the values of density known for 20°C. Propyl is 9 percent in error. The purpose of the exhibit in Table I is to show a consistency in the interpretation and only to this extent is the evidence confirmatory.

TABLE I

Densities of alcohols.

alcohol	computed ρ	actual density	1.2ρ
Methyl	0.653	0.792*	0.783
Ethyl	.625	.789*	.747
Propyl	.612	.804*	.734
Butyl	.654	.810*	.784
Amyl	.680	.817*	.816
Hexyl	.702	.820*	.842
Heptyl	.714	.817‡	.856
Octyl	.718	.827*	.861
Nonyl	.710	.828*	.852
Decyl	.709	.830*	.850
Lauryl	.714	.833*	.856

* At 20°C, ‡ at 22°C given by International Critical Tables.

The arrangement of molecules discussed, the computations in accord therewith, and the comparison with other evidence, should be regarded as convincing evidence of the cybotactic state.

Structure not crystalline. There are several reasons that lead to the rejection of the theory of fragmentary crystals[19] in liquids as the basis of explanation in the alcohol experiments. First, the crystal theory does not agree with our general views of the two states, solid and liquid. One can understand that the solid state may depend upon a critical temperature or melting point, but it is not clear why, under the same view, any fragments of crystal should remain. A second objection to the fragmentary crystal theory is such experimental evidence as is shown in Fig. 4. The position of the diffraction peaks in solid lauryl alcohol are at 1.0°, 9.7° and 11.0°, and in the liquid are at 1.65° and 8.8°. Obviously, the computed grating spacings are not the same. Stated in the same order, they are, 35.6, 4.2, 3.7; 24.7, 4.6, in Angstrom units. One of the distances has been increased by melting and the other decreased. The structure in the solid and in the liquid may have similarity, but they cannot be the same. Hence, the groups in the liquid are not merely fragments of the crystals in the solid. As a third aspect, con-

[19] See Hewlett, ref. 3, Hückel, ref. 8, and A. H. Compton, Bull. Nat. Res. Council, No. 20.

sideration should be given to the resolving power of fragmentary crystals. The literature [20] provides a formula for the breadth of a line in terms of the wave-length and size of the crystal fragment. It is $h = 2(\ln 2/\pi)^{1/2}\lambda/\Omega$ $(\cos \theta/2)^{-1}$ wherein h is the breadth of peak half way from base to maximum, λ is the wave-length, Ω is the length of edge of the cubic crystal. The value of h in lauryl, for example, can be obtained from Fig. 2. It is $3°$ at $\theta = 8.8°$ giving Ω a value of about 14×10^{-8} cm. Inasmuch as this is less than the length of one of the spacings, one is not encouraged to find the explanation of the peak breadths in the size of the supposed crystal fragments. Even the assumption that there are two distances concerned instead of one, would not essentially modify this view.

The discussion above given concerning the arrangement of the molecules is presented, not as proof, but merely as an indication of the essential correctness of the view of the cybotactic state here put forth. *The important conclusion is that a space array exists* and that it depends upon the carbon content somewhat in the manner indicated.

Absence of second order. In the present experiments second order maxima are not found. This is not surprising. If diffraction does not occur in crystals but in an oriented state not so fixed in form, the second order would probably be relatively less in intensity than with crystals. A careful effort has not been made to detect the second order, but it certainly is less than 5 percent of the first order. Fig. 2 suggests that with lauryl a sharper peak and a trace of second order exist. Only the former seems certain at the present stage of the experiments.

Surface Effect. One might readily conceive of the cybotactic state as caused by the presence of the surface of the glass cylinder in which the liquids are placed. That this is not true was shown by varying the diameter of the cylinder three-fold, yet with the beam narrower than the diameter. In each case the surface exposed to the x-rays was approximately the same. But the observations showed that the diffracted beam altered with the volume, and in a manner to be expected from computations of optimum thickness. Moreover, the relative magnitudes of the two diffraction peaks remained approximately the same with the variation in diameter. From these observations, the hypothesis of a surface phenomenon as responsible is untenable.

Cybotatic state. As indicated in the introduction to this paper, one cannot readily accept the view that the atomic and molecular forces undergo discontinuities at the melting point. But the resulting stability may be critical at this temperature. The molecular arrangement that was stable in the crystalline form may approximate the most probable grouping in the liquid state. In the former there is rigidity of form, but in the latter there is mobility. In both the molecular vibrations are those of acoustic waves. Throughout the liquid at any instant there are scattered many small groups having the spacings reported herein. Over any appreciable time, there are a greater number of these groups than of groups having spacings of any other adjacent values. These groups do not retain their identity. Our diffraction

[20] P. Scherrer. Nachr. d. Konig. Gesell. d. Wiss. at Göttingen, 1919–19, p. 98.

curves have broad peaks not only through the minute size of these groups but also because there is a wide distribution of values of the distances among the organized groups. The above description regards the latter as the more important factor in the diffraction result.

An attempted discussion in detail of these molecular groups would be premature. Nevertheless it is important to point out the similarity of the breadth of the chief peak of the diffraction curves of the alcohols from hexyl ($C_6H_{13}OH$) to lauryl ($C_{11}H_{23}OH$). The breadth cannot be determined by the size of the group, for it would seem that the doubling (almost) of the molecular length would materially change the size of a group. But the evidence of our results taken in entirety points to the inapplicability of resolving power as dependent upon size. The positions of the molecules are not sufficiently stable to apply a crystalline theory.

It is important that a differentiation between the cybotatic and the crystalline states be definitely drawn. Each refers to an organization of molecules. In each the organization depends upon the nature of the molecules as expressed in molecular forces. But one is fluid and the other solid. The analogy between the two does, however, give a clear conception of the nature of a solution. We know that in solid alloys, the atoms of the alloying material participate in the crystal lattice of the metal alloyed. It is a solid solution. *In a liquid solvent, the solute is "dissolved" in that it participates in the organized grouping of the solvent.* If it does not so participate it is a foreigner and might be called a *colloid*. This suggestion gives a helpful conception of a solution.

Universality of cybotaxis in liquids. A general conclusion of the universality of cybotaxis in liquids is not justified, but certainly the hypothesis is a very attractive one. It is noticed that, as the molecule becomes shorter, its group organization, as shown by the width of the 4.6A peak in Fig. 3, follows a more widely distributed probability. In fact the diffraction curve more and more resembles that of water as the molecule becomes more nearly the shape of that molecule. Our present x-ray method does not show the cybotatic state clearly unless it becomes strongly marked by the use of long chain molecules. Nevertheless, cybotaxis appears to be of importance with any liquid. This is indicated by latent heat of vaporization values.

A large portion of the observations in this paper were made by Mr. Wm. D. Crozier, the research assistant of the first named author. His splendid aid is gladly acknowledged.

This study of liquids is being continued with acids, with paraffins, and with various isomers.

PHYSICS LABORATORY,
    UNIVERSITY OF IOWA.
        June, 1927.