

X-RAY DIFFRACTION IN WATER: THE NATURE
OF MOLECULAR ASSOCIATION

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ABSTRACT

The x-ray diffraction intensity-angle distribution for water and its variation for a temperature of 2° to 98° C, are given. Two important periodicities of 3.24 and 2.11A and a third of 1.13A at 21°C are established in satisfactory agreement with Meyer. The first one *decreases* with increasing temperature and the second *increases*.

It is shown that the conception of molecular complexes explains neither the existence of these periodicities nor their change with temperature. In fact, the description of "association" that involves complexes of two or three or more molecules, should be abandoned in favor of the molecular group conception, (cybotactic condition) emphasized by the author. These groups of molecules containing hundreds and perhaps thousands of molecules in each, have a temporary existence as individuals, have ill-defined boundaries, possess an optimum size and an internal regularity determined by the temperature and molecular forces, and expand anisotropically. The experimental facts are in agreement with this view. A detailed description of the molecular arrangement in water from x-ray data is not at present possible yet it simulates the crystal arrangement in ice. A mathematical treatment of the forces within and between the molecules in such groups can probably be studied with much profit only from the quantum viewpoint.

THE nature of water has received a great deal of attention, not merely because it is the most important liquid, but because its physical properties are unusual. The present paper is not an attempt to discuss the various theories¹ concerning the constitution of water. Its purpose is to give the results of x-ray diffraction studies and to emphasize the conclusions directly toward which these studies, as well as those of other liquids, seem to point.

The examination of crystals by x-rays has shed distinctly new light upon the structure of the solid state. Its method of examination is simple and direct, being based upon both classical and quantum theories, and there seems no doubt but that the space periodicities of concentration obtained by the applications of Braggs' law is correct. During the past few years many liquids have been examined by x-ray diffraction and the conclusion is becoming increasingly strengthened that here, too, the space periodicities may be determined.² Indeed, these periodicities, which are clearly made evident by the diffraction experiments, seem to be caused by an approximately orderly space array of molecules in small groups having ill-defined boundaries and temporary individual existence. These groups are not sparsely distributed, but occupy the greater portion of the volume, as can be shown

¹ For a resumé see H. M. Chadwell, *Chemical Reviews* **4**, 375 (1927).

² See Stewart, *Phys. Rev.* **35**, 726 (1930).

by a comparison of intensity in the liquid and powdered crystal state.³ Their magnitude appears to be of the order of hundreds or thousands of molecules, but no exact measurement has been made. The closest approach to such a measurement at present is contained in the experiments of McFarlan⁴ which show that an electric field will produce increased orientation of molecules of nitrobenzene to an extent that is far greater than would be expected from the orientation of independent molecules. The effect is so small that computations should perhaps await further data.

EXPERIMENTAL RESULTS

A full description of the apparatus and precautions may be found⁵ in an earlier article. The $\text{MoK}\alpha$ doublet radiation was used, being partially isolated by the use of a zirconium oxide filter. In Fig. 1 is shown an x-ray diffraction intensity-angle curve for powdered crystals of triphenylmethane. This shows, because of the comparative isolation of the line at 9° , the small amount of

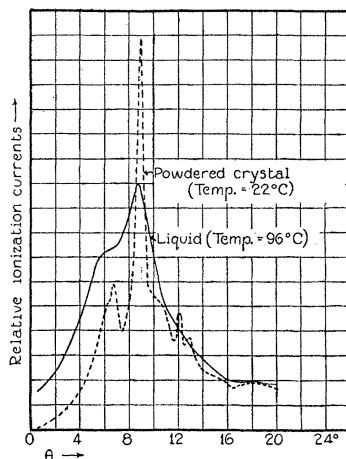


Fig. 1. X-ray diffraction curves for equal masses per unit area of triphenylmethane in liquid and powdered crystal forms.

general $\text{MoK}\alpha$ radiation present. The general radiation is in evidence in the general elevation of the crystal curve. The maximum in the general radiation is about 6° , but the errors caused thereby, as indicated by Fig. 1 are small. A higher voltage would probably increase the general radiation to an undesirable extent. It is also to be borne in mind that the thickness of the specimen of water used was less than 1 cm or less than the optimum thickness. By this second precaution any accentuation of the general radiation by differential absorption is avoided.

³ For example, see Fig. 1 wherein the same mass of material is used. The integral intensity in the liquid case is comparable to that of the solid.

⁴ R. L. McFarlan, *Phys. Rev.* **35**, 12 (1930).

⁵ Stewart and Morrow, *Phys. Rev.* **30**, 232 (1927).

Fig. 2 shows the uncorrected results of Meyer⁶ by the broken line and those of the author by a continuous line. Meyer used a strictly monochromatic radiation obtained by crystal reflection. When the corrections of Meyer are made the alterations occur chiefly at the larger angles. Meyer's method was that of photography while that of the author was the ionization effect. Meyer used a stream of water and the author a thin walled glass tube as a receptacle. His monochromatic radiation gives his curve the greater quantitative weight.

Earlier diffraction experiments with water give the results presented in a foot note.⁷ But none had found more than one peak until the careful work of Meyer just cited.⁸

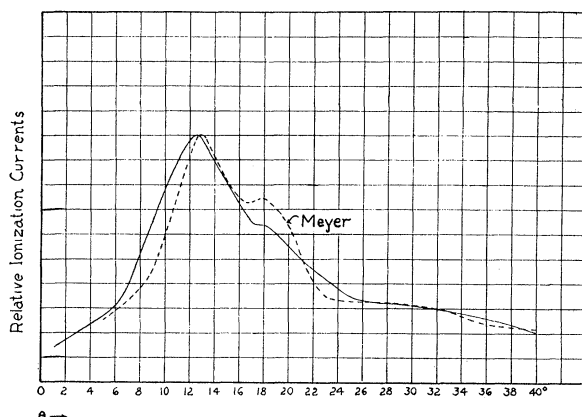


Fig. 2. Diffraction intensity of water, giving comparison of Meyer's uncorrected monochromatic curve with that of the author's. Temperatures 20° and 21°C respectively.

Fig. 3 presents the results for the change in temperature from 2° to 98°C. The tube was heated by hot (and cold) air blasts in such a manner as to prevent the introduction of any scattering material in the path of the x-rays. The temperature as given is correct to within 1.5°C throughout the entire range.

An additional experimental result must be mentioned, though it is not presented in detail because used only as a check experiment on known data. Diffraction curves were obtained with powdered ice, produced by plunging

⁶ H. H. Meyer, *Ann. d. Physik* **5**, 701 (1930).

⁷ Sogani, *Ind. J. Physics* **I**, **IV**, 357 (1927), has one value, 3.27Å; Krishnamurti, *Ind. J. Phys.* **II**, **IV**, 491 (1928) has one value, 3.26Å; Keesom in *Physica*, p. 118 (1922) and Keesom and de Smedt, *Proc. Royal Soc. Amsterdam*, **25**, 118 (1922) and **26**, 112 (1923) give the values 3.05Å in the first two references and 3.04Å in the last. *Prins Zeits. f. Physik* **56**, 617 (1929) gives one value, 3.1Å. He raised the temperature to 80°C with no noticeable alteration.

⁸ The author's experimental work preceded the publication of that of Meyer. The former was presented at the April, 1930 meeting of the American Physical Society and described by abstract only in the June 1, 1930 number of the *Physical Review*. Probably Meyer's article appeared in print a little later, the number of the *Annalen* reaching the author on July 29th, 1930, but Meyer's work was described in full at that time.

the glass tube receptacle in liquid air. The diffraction curves for two samples were in fair agreement and showed relatively prominent lines at approximately 10.5° , 11.7° , 18° and 19.5° . Dennison⁹ used a Mo target and zirconium filter and found the most prominent lines to be at (1) 11.16° , (2) 19.86° , (3) 11.88° and 30.2° , (4) 15.3° and 27.16° , (5) 10.44° and 18.12° and 21.38° , the relative values being 10, 5, 2, 1.5, and 1, respectively. It will now be seen that the liquid peaks at 12.5° , 19° and 31° in Fig. 3 correspond approximately with the most intense lines found by Dennison in an extended in-

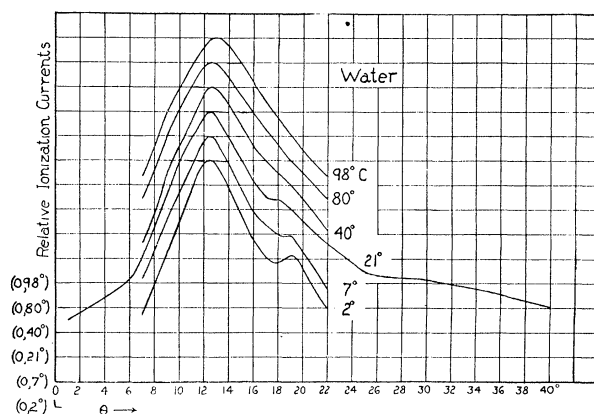


Fig. 3. Displaced diffraction intensity curves of water at different temperatures.

vestigation, and by the author in the brief tests described, in the same apparatus as was used for water. In this approximate correspondence of liquid to solid state H_2O does not differ from other compounds.¹⁰ For example, see the liquid and crystal curves compared in Fig. 1. In case of no substance yet tried do the peaks of a liquid exactly correspond with the lines of the solid, and the difference is not a temperature one. It is evident that such periodicities as are found in the liquid state have strong quantitative similarity to the most important of those in the solid state.

CONCLUSIONS

There are several conclusions to be made directly from Fig. 3 and the foregoing assuming that Bragg's diffraction law gives the distances of separation in the periodicities represented by the peaks. Further, it is simplest to assume that these distances, 3.24, 2.11 and 1.13A, corresponding respectively to angles 12.5° , 18.8° and 31.0° of Fig. 2, or, at least the first two, correspond to molecular separations. This assumption is in accord with experiments with other liquids and with the similarity of liquid to solid state. H. H. Meyer gives as his results at $20^\circ C$, 3.13, 2.11 and 1.34A. With the assumptions cited, the conclusions are as follows:

⁹ Dennison, *Phys. Rev.* **17**, 20 (1921).

¹⁰ See list of eight liquids given by Krishnamurti, *Ind. J. Phys.* III, **II**, 225 (1928). The present author has tested three additional ones.

1. The distance between molecules (scattering centers) represented by the most prominent peak decreases with temperature, whereas the distance corresponding to the next most important peak seems to increase. H. H. Meyer gives a decrease for the former of 0.0018Å per °C, whereas our results show 0.0014Å. He obtains a constant position for the second peak.

2. The second peak disappears with increasing temperature. H. H. Meyer showed at 40°C a reduction to two-thirds the value at 3°C.

3. The breadth of the large peak increases with increase in temperature.

4. There is a quantitative similarity between the periodicities found in the liquid and the three most prominent periodicities found in powdered ice.

A few years ago the reader might have concluded at once from Fig. 3 that therein is additional evidence of the complexity of the molecules and of the disappearance of one or more complexes with increasing temperature. But the evidence of to-day would indicate at once the incorrectness of this position. For x-ray diffraction experiments indicate that when two liquids are completely miscible in the proportions used, the marked periodicity found in the solution is not that of either constituent alone, but distinctly of the solution. This has been shown by Krishnamurti¹¹ with glycerine, ethyl alcohol and lactic acid in an aqueous solution. Meyer¹² used solutions of n-ethyl alcohol and methyl cyclohexane, n-butyl alcohol and orthodimethyl cyclohexane, quinoline and phenol, cyclohexane and tetranitromethane and phenol and water. As an illustration of results, each of the first four mixtures used by Meyer showed but a single periodicity and this was intermediate between the periodicities of the liquids examined separately. These mixtures were totally miscible. The phenol-water mixture showed the same effect when not an emulsion. As an emulsion the two peaks of the constituents were found. The evidence shows that, without exception, two liquids, totally miscible, in solution will show a grouping of molecules (a periodicity) that is not that of either one. It is, therefore, highly probable that, if there were two "complexes" in the water in our present experiment, they would be totally miscible and would not show their individual periodicities. Hence, we may safely conclude that the two peaks in the water diffraction curve correspond to periodicities of *one kind of molecular grouping and one kind only*. The complex molecule interpretation suggested at the beginning of this paragraph is not, therefore, tenable. Moreover, it cannot be claimed that the diffraction peaks with ice indicate several complexes. They correspond to the periodicities in one molecular grouping, one crystal structure. Yet the liquid peaks have a striking similarity that is not explained by the introduction of several complexes but rather, as in ice, by periodicities in one grouping.

Langmuir¹³ pointed out a number of years ago that liquids are very much more nearly like solids than like gases. Consider density, compressibility, temperature expansion, specific heats, refractive indices, other

¹¹ P. Krishnamurti, Ind. J. Physics **III**, 331 (1929).

¹² A. W. Meyer, not yet published in full; abstract, Phys. Rev. **35**, 291 (1930).

¹³ Langmuir, J. Am. Chem. Soc. **39**, 1848 (1917).

optical properties, etc. The only essential difference between liquids and solids is that of fluidity. This one difference has had much to do with the hasty conclusion, held for many years, that the arrangements of molecules in a liquid are as irregular as in a gas. Now we learn from x-ray diffraction experiments that the liquid does have a crude regularity in multitudinous groups, an irregularity of orientation of these groups, and an irregularity of molecules between these temporary groups. With this view it would appear that the simple explanation of molecular association is the association in groups of a relatively large number of molecules and not in complexes consisting of two, three, etc., molecules. The number of molecules in a cybotactic group has not been determined, but one would expect it to be from several hundred to several thousand. Fig. 1 shows that these groups give as much scattering as powdered crystals of the same mass. The groups must therefore be practically everywhere present.

The physical chemist introduced the conception of complexes to account indirectly for the data of vapor pressure, boiling point, latent heat, viscosity, surface tension, etc.¹⁴ But the study of crystals points very clearly to a similarity of crystal forces and internal molecular forces, and gives ample reason to expect that liquid molecules in groups as described must act differently than molecules that are more nearly free as in a gas. Consequently, what formerly has been attributed to forces between molecules in a complex are now seen to be the forces within the groups causing the regularity of arrangement.

Arrangement of molecules in the groups. In order to make the description of "association" more definite, a brief discussion will be given of the present status of the group arrangements.

The arrangement of polarized molecules is not, for example, as suggested illustratively by Debye,¹⁵ the minimum potential configuration of two spheres (molecules) with idealized doublets of infinitesimal length at the centers, thus forming a double molecule with axes of the two doublets in line joining the centers of the spheres. Neither is the arrangement determined solely by the electrical effect of the doublets. With reference to the first point, the experiments in n-alcohols,¹⁶ isomers of n-alcohols,¹⁷ and normal saturated fatty acids,¹⁸ show that when the OH or OOH group is at the end of the chain two groups are adjacent in two molecules having their chain lengths lying in the same straight line. That is, the molecules are arranged head to head (the polarized group) and tail to tail in parallel lines continuing over a group of molecules. The doublets appear at the heads and not centered in the molecule. Moreover, the head to head junction is arranged in an orderly manner with other such junctions in the adjacent parallel lines, so

¹⁴ See Turner "Molecular Association" Longmans, Green and Co., 1915 and Longinescu, Chem. Review **4**, 381 (1929).

¹⁵ Marx Handbook der Radiologie **VI**, 597 (1925).

¹⁶ Stewart and Morrow, Phys. Rev. **30**, 232 (1927).

¹⁷ Stewart and Skinner, Phys. Rev. **31**, 1, (1928).

¹⁸ Morrow, Phys. Rev. **31**, 10 (1928).

that their location forms a definite longitudinal periodicity recognized by x-ray diffraction. The planes associated with these junctions are not normal to the chain lengths. When the polarized OH group is attached not at the end of a chain but removed therefrom by at least one carbon atom,¹⁹ then the double arrangement disappears and the longitudinal periodicity referred to now occurs at a distance corresponding to the length of one molecule and the associated planes are normal to the chain lengths. At the same time the periodicity caused by parallel arrangement of molecules remains. It is to be noticed in the above pictures, we do not have double molecules and the association is that in a group, indeed, similar to the situation in a crystal. The original papers should be consulted for the evidence of the longitudinal grouping and the interpretation of it. So far the grouping (or association) may appear to be regarded as caused primarily by the electrical forces of the doublets. But this is not correct, for it does not account in general for the parallelism of chain molecules. A direct experiment is with n-paraffins.²⁰ Here the molecules lie parallel and yet they are unpolarized.²¹ We are dealing with other intermolecular forces than those due to doublets. In geometric language the "shape" determines the grouping to no small extent. With the paraffins there is no periodicity in the longitudinal direction as with the n-alcohols, etc., and it is evident that this periodicity of the last named may be regarded as caused by the presence of the doublets.

The detailed arrangement of molecules in other than long chain liquid compounds is not ascertained readily by x-ray diffraction, for the lack of approximately perfect regularity in the groups makes the detectable number of periodicities too small. Thus, in the case of water no further conclusion as to detail can be made than already stated. The periodicities are evidently quantitatively similar to the most prominent ones in ice, but this does not, of course, mean like arrangement.

The above discussion states that what was formerly regarded as the peculiar association of two, three or four molecules, as the case may be, now loses its identity in the orderly group formation of molecules. If this be correct, then, since the values formerly computed for the average number of associated molecules change with temperature, there should be evidence for the alteration of the groups with temperature. This proves to be true. Skinner²² found with a group of liquids that there were changes in the dimension of the periodicity that could not be accounted for by expansion. Similarly, in Fig. 3, it is shown that one such distance increases with temperature while the other decreases. Since neither isotropic nor anisotropic *expansion* accounts for the effect, it may be assumed that there doubtless may occur temperature changes in the molecular forces caused by alterations in molecular "shape," or essentially in the precise arrangement of atomic centers in the molecule. Skinner also showed that in certain cases the in-

¹⁹ Stewart, Phys. Rev. **35**, 726 (1930).

²⁰ Stewart, Phys. Rev. **31**, 174 (1928).

²¹ R. W. Dornte and C. P. Smyth, JI. Am. Chem. Soc. **52**, 3546 (1930).

²² Skinner, Phys. Rev. **36**, 11, 1625 (1930).

tensity of the x-ray halo *increased* with increasing temperature. This also suggests alteration in grouping.

The x-ray study is not the only experimental evidence of such internal alteration. We know, for example, that when there are changes in magnetic moment as occurs, for example, in para-azoxyanisol, there must be internal changes in the molecule.

The group conception, as given above, seems to be in harmony with all the facts. On the other hand, there are good reasons for the abandonment of the theory of complexes. Reference to a recent contribution of G. G. Longinescu,²³ who has been an active contributor in this field, will satisfy the reader upon this point. The most important reason for turning from the older conception is that it has proved unprofitable and does not longer serve any useful purpose in stimulating new contributions. Its extended use has increased the inconsistent results and it has ceased to be even empirically satisfactory.

The new conception here proposed seems to be helpful in several respects. First, it suggests that experiments based upon the theory of complexes will not prove profitable and recommends their abandonment. Second, it states that the secret of association lies in an understanding of those forces, call them chemical or physical as one will, which bind atoms together in a molecule and which cause stable configuration in crystals and unstable arrangement in liquids. If, as at present appears, such an "understanding" will only be had through the development of quantum theory, these forces being studied by the energy levels obtained in radiation and absorption spectra of constituent atoms and molecules, then a physical description of the origin of these forces appears improbable. They will appear to exist only because of atomic and molecular energy levels,²⁴ and the resulting energy changes. They cannot be understood by distributions of electricity and the application of electrical laws. That has proved unsatisfactory even for the simplest atoms. In any event, the cybotactic group conception of association removes the difficulties inherent in molecular complexes and will prove helpful in a study of the nature of the liquid state.

I desire to express appreciation for the experimental skill of Mr. H. A. Zahl, research assistant, who is responsible for the observations involved in this report, and thanks for a supply of conductivity water to Professor J. N. Pearce of this University.

²³ Longinescu, *Chemical Review* **6**, 381 (1929). See also J. W. Williams, *Chemical Review* **6**, 589 (1929) and particularly p. 614 *et. seq.*

²⁴ See Langer, *Phys. Rev.* **34**, 92 (1929).