X-RAY DIFFRACTION IN LIQUIDS

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X-ray Diffraction in Liquids

I. HISTORICAL

Debye and Scherrer showed in 1916 that passage of a pencil of x-rays through a thin unenclosed stream of liquid produced a broad halo surrounding the central undeviated beam. They established the phenomenon as interference by comparing the diameter of the ring when using different wave-lengths. In 1922, Keeson and de Smedt identified weak secondary haloes for oxygen, argon, and nitrogen, in the liquid states. In the same year Hewlett examined benzene, octane, and mesitylene, contained in thin celluloid capsules, by the spectrometer ionization method. He showed that the scattering at small angles is small. Since that time considerable work has been done on this phenomenon, especially by Raman, Stewart, Prins, Debye and their associates. By all, it is agreed that the diffraction effects indicate spatial orderly arrangement of molecules.

II. CURRENT THEORIES

1. Raman's Theory.

The first serious attempt to explain the diffraction of x-rays by liquids was made by Raman and
Ramanathan in 1923. The approach is similar to that of Smoluchowski and Einstein in the scattering of visible light by liquids. The liquid is considered continuous as a whole but subject to local fluctuations in density. The assumption of continuity is valid in the case of visible light because of the large difference between the wave-length of light and the size of a molecule; but this is not the case with x-rays.

The statistical-thermodynamical considerations can be applied directly when the angle of scattering is small. For larger angles, it is necessary to find an expression for the local variations of density. For the intensity, Raman gets

\[ I = C \exp \left\{ -\frac{1}{lo} \frac{\lambda}{4\pi} l_0^3 \left( 1 - \frac{\sin^2 \Theta}{\sin^2 \Theta_o} \right) \right\} \]

where \( l_0 \) is the mean distance between neighboring molecules and given by Bragg's equation \( \lambda = 2l \sin \Theta \), \( \beta \) is the isothermal compressibility of the fluid, \( \Theta_o \) is the half diffraction angle for the principal halo, and \( \Theta \) for any scattering angle.

If \( I \) is plotted against \( \frac{\Theta_o}{\Theta} \), the sharpness of the maximum depends upon \( \frac{l_0^3}{\beta^3} \). The curves for water and glycerine correspond fairly well with those obtained experimentally, but the agreement is not so good for ether. In the latter case the large value of \( l_0 \)
makes the theoretical curve sharp whereas the experimental curve is broad. The theory has been widely applied by Raman's associates to explain the effect of change of temperature and concentration of solution on the rings. No account is given for the two or three diffraction bands of some liquids, however, so the theory can be no more than an approximation to the truth.

2. Stewart's Theory.

A crude idea of the liquid as a mass of fragmentary crystals had been suggested soon after the phenomenon attracted attention. Keeson and de Smedt and Hewlett made this hypothesis more logical by assuming a kind of temporary crystallization. The atoms or molecules would imitate, over short elements of space and time, the arrangement of the crystalline state. This may have been the beginning of Stewart's theory.

Stewart explains the diffraction pattern on the basis of molecular grouping which he calls cybotaxis. At any particular instant small orderly groups of molecules exist at various points in the liquid. The volume occupied by grouped molecules will depend upon the substance under consideration. The molecules do not remain permanent members of any one well defined group but are continually moving from one to another.
The cause of this molecular grouping is attributed to the shape of the molecules. If the molecules were cigar-shaped, parallel grouping would be more probable than any other owing to the nature of the molecular forces. The kinetic energy of the molecules will not necessarily disturb the cybotactic state for it has been shown that the relative velocities of any two adjacent molecules may be small, in comparison with the actual velocity of either.

As the temperature of ether is increased it has been shown that the maximum scattering intensity is shifted toward smaller angles and the peak heights decrease. The shift is attributed to thermal expansion which would produce an increase in spacing and hence make the maximum occur at a smaller angle. The decrease in peak height is caused by an increase in thermal agitation which would make conditions less favorable for the existence of cybotactic groups. The scattering at small angles is proportional to the number of random molecules and hence increases with rise in temperature. At the critical temperature the liquid and vapor phases merge and the cybotactic group formation ceases to exist. Ordinarily a liquid mixture will give a diffraction pattern on which the patterns of the two components are superimposed. If the two liquids are completely miscible,
however, the diffraction pattern is different from either constituent. The main peak has an angular position between the peaks of the constituents and shifts directly with the concentration. This indicates a single type of cybotactic group formed by molecules of both groups. The x-ray pattern may thus be used to distinguish between different types of liquid mixtures.

The variation of gas viscosity is fundamentally different from that of liquids. The former increases with rise in temperature, the latter decreases. Andrade develops a theory for liquids on the basis of momentum transfer taking place during a temporary union of molecules. The conception is thus similar to that of Stewart’s. Stewart and Edwards have found an unmistakable correlation between the coefficient of viscosity and the perfection of grouping for chain molecules as shown by x-ray diffraction. The cybotactic condition may therefore be a satisfactory basis for explanation of liquid viscosity.

3 Debye’s Theory.

Debye assumes that the diffraction is caused by neighboring molecules. He derives a distribution function for the arrangement of the molecules in a liquid. The maximum scattering angle is defined by the quotient of the wave-length of the radiation and the diameter of
the sphere occupied by the molecule. The curves are only approximate but the scattering angle is of the right order or magnitude for simple molecules.


This theory is also largely mathematical. A distribution function is assumed and evaluated in an empirical way. To apply the theory, the liquid is assumed to consist of spherical atoms closely packed together so that the free space is negligible. A reasonably good agreement with the experimental intensity curve for mercury is obtained. The approximate nature of this assumption limits the application to monatomic liquids.

The possibility of a comprehensive theory for liquids, as exists for gases, seems to be in further study of x-ray diffraction patterns. What is needed most, perhaps, is information on the diffraction of some simple substance in all three states and at different temperatures.

III. EXPERIMENTAL.

1. Transformer.

The transformer consists of two 50,000 ohm secondary coils wound on a 0.25 ohm primary and the whole immersed in oil. The primary is tapped in two places so three connections are possible.

<table>
<thead>
<tr>
<th>Connection</th>
<th>Resistance</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 1</td>
<td></td>
<td>0.231   ohms</td>
</tr>
<tr>
<td>0 - 2</td>
<td></td>
<td>0.242</td>
</tr>
<tr>
<td>0 - 3</td>
<td></td>
<td>0.255</td>
</tr>
</tbody>
</table>
A rheostat of 12 ohms is placed in series with the primary when starting since the instantaneous current in the x-ray tube may be large.

The secondary coils are connected to the primary (terminal 3) to prevent sparking between the inside layers of the former and the outside layers of the latter. This allows an efficient and compact transformer but is rather unfortunate in this case. Since the target end of the x-ray tube must be grounded and one side of the 110 volt a.c. supply is also grounded only half of the transformer can be used. Thus the voltage available was only 35,000 when the full 70,000 volts would have been much better. An ammeter, reading up to 20 amperes, is placed in the primary circuit and a milliammeter, with a maximum of 12 milliamperes, is in the secondary circuit.

2. X-ray Tube.

The x-ray tube is of the Shearer type, which is the most suitable for the study of diffraction effects. The three most important advantages are: (1) replaceable targets, (2) water cooling, (3) aluminium window. The first enables one to change the wavelength of the x-rays, the second allows continuous operation, and the third increases the intensity of the rays by giving less absorption and by permitting the
spectrometer to be placed nearer the target. The tube has considerable rectifying properties so the transformer can be connected to it directly. The cathode end is cooled by convection in a long, insulated brass vessel filled with water.

The x-ray tube is evacuated by means of a mercury pump and an oil back pump. Since the operation of the tube depends upon the ionization of the air by fast electrons, too low pressure is possible. The artificial leak used consisted of a variable needle valve connected by rubber tubing to a jar evacuated by the oil pump alone. The right order of leak was obtained by making a number of small needle holes in the rubber tubing; fine adjustment of the pressure could then be made with the needle valve. Heavy stop cock grease is needed for the threads of the valve. This arrangement keeps the pressure constant at the right value for six hours or more as shown by the reading of the milliammeter.


The Dr. Müller x-ray spectrograph is suitable for the study of x-ray diffraction by liquids as well as by crystals. The arrangement is nearly the same as that for the Laue spot method of investigating crystal structure. The x-ray beam is limited by a narrow cylindrical channel
in a brass rod, which has one end about 4 mm from the aluminium window and the other 2 to 3 cm from the liquid. The plate holder is 5 cm on the other side of the liquid. Black paper covers the face of the plate holder so plates may be taken in daylight. A small circular piece of lead prevents fogging of the plate owing to the direct beam.

The cell used for containing the liquid seems to be a distinct improvement over others that have been used. The liquid is contained between two mica windows 1.5 mm apart. The mica is held in position by a ring of brass on each side of the centre piece. The three rings are clamped together with six screws. The liquid to be examined is poured into a brass cylindrical vessel above the cell and the liquid enters the cell by small metal tubing 1 mm in diameter. The whole is supported by an iron rod 7 cm. long which fits into the centre of the spectrograph table.

The advantage of using mica windows is that no ring is given by this substance, as is the case with glass and metals, but only spots which do not interfere
with the ring given by the liquid. The method of clamping enables one to clean the cell easily and to change the windows. A special cutter was constructed for cutting out mica windows 10 mm in diameter and 0.01 mm thick. The vessel on top is convenient when filling the cell and also makes it easier to examine liquids with high vapor pressure at room temperature. By placing a little stop cock grease around the cover on top liquids such as cyclohexane and ether may be contained in the cell for several hours. The supporting iron rod screws into the cell so that the height may be adjusted until the beam of x-rays passes through the centre of the cell.

4. Experimental Procedure.

Having chosen the target desired (copper was used throughout this experiment) and having properly put it in place with a little stop cock grease, the tube is evacuated. An electric heater for the mercury pump is most convenient but it takes about 20 minutes to heat the mercury sufficiently. The pressure in the tube can be estimated by the color and the ammeter reading. The current is slightly positive as the purple glow gradually extends along the cathode. As the glow fills the tube and striations appear the current shifts to the negative. The glow recedes and finally disappears
almost completely. The current shifts abruptly from a strong negative to a strong positive reading (about 12 m a) and x-rays may then be observed with a phosphorescent screen. The current is kept from decreasing beyond 6 or 8 m.a by means of the artificial leak.

The spectrograph is adjusted, by looking through the small circular hole, until the cell and lead shield on the plate holder are in proper alignment. The spectrograph can be put into the correct position to allow maximum intensity of x-rays through the circular hole by using a zinc sulphide phosphorescent screen.

The liquid is put into the cell and a plate exposed for six hours. A shade was made for the window so the plates could be developed in the same room. It is desirable to have the room dark, also, when using the phosphorescent screen. Fogging of the plates was prevented to some extent by surrounding the entire spectrograph with lead.

5. Discussion of Results.

Eighteen liquids have been examined and all show marked differences in the diffraction patterns. Many of the patterns are very faint but a sample of eight is shown. An explanation of the observed effects will be attempted in terms of Stewart's theory. This theory is chosen because
it gives the most complete picture and because the mathematical theories are still very limited in application.

1. Benzene and Cyclohexane.

These two diffraction patterns are very similar in both size and sharpness of the ring. The two liquids have similar structural formulae; hence it would seem that the shape of the molecule is involved in the formation of cybotactic groups. The distance between groups and the number of groups per unit volume is then determined by the shape of the molecule. In both cases, the number of molecules in groups as compared to the number not in groups must be great; for the scattering at small angles given by random molecules is very weak. Why this benzene ring should give such an orderly arrangement of molecules is difficult to see.

There is a striking difference in intensity, however. When the double bonds between the carbons in benzene are replaced by a single bond and an additional hydrogen in cyclohexane we get a great increase in intensity. Thus the arrangement $\text{H}_\text{C}^\text{C}_\text{H}$ seems to be much more effective in scattering x-rays than $\text{H}_\text{C}^\text{C}_\text{C}$. The change in intensity might be due to the addition of more hydrogen ($\text{C}_6\text{H}_{12}$ as compared to $\text{C}_6\text{H}_6$) but it is doubtful if the explanation is as simple as this.
2. Ethyl Alcohol and Ether.

These two liquids differ in that ethyl alcohol has one ethyl group per molecule while ether has two. Two explanations seem possible for the ether ring being smaller and more diffuse. The ether cybotactic groups are fewer and farther apart because the shape of the molecule is different or because the ether was nearer its boiling point. It is to be noted that the boiling point of benzene and cyclohexane are about the same ($80^\circ C$) so no difference in size or diffuseness of the ring would result in that case. Ether, however, boils at $35^\circ C$ while alcohol boils at $78^\circ C$ at atmospheric pressure. The latter explanation seems most probable but further investigation on this point is necessary.

The diffraction by ether is more intense than that by alcohol. It would seem that, if replacing a carbon bond of hydrogen is effective in increasing the intensity, replacing the hydrogen by an ethyl group is even more so. This hypothesis is borne out in the next two plates in which hydrogen in acetic acid is replaced by an ethyl group in ethyl acetate and the intensity thereby increased.

3. Acetic Acid, Ethyl Acetate, and Ethyl Malonate.

When acetic acid and ethyl alcohol combine to form ethyl acetate we get an x-ray diffraction pattern
quite different from either of the original materials. The new ring is not a combination of the other two since the ethyl acetate ring is the smallest. The distance between cybotactic groups has been increased while the number of groups, as shown by the broadening of the band, has been decreased.

Ethyl malonate is different from all the other patterns shown in there being two rings distinctly visible. The outer ring is similar in size and appearance to ethyl alcohol. It would be interesting to see if the inner ring is similar to malonic acid. In any case, the combination of ethyl alcohol and malonic acid has resulted in a compound which has a dual cybotactic arrangement. Two types of group combination must be occurring.

4. Pilchard Oil.

The very distinct ring given by pilchard oil is interesting. Fish oil is a mixture of unsaturated (i.e., double or triple bonds between the carbons) glycerol esters. Since complicated long chain molecules exist in this substance, the diffraction may be caused by regularity in the arrangement of the atoms in the molecule rather than by regularity of the molecules in the liquid. Thus each molecule would act as a small crystal. This should be
possible when the molecules are several times the wavelength of the light used. If this is the cause of the 'ring we should expect it to be sharp since the number of regular arrangements would be greater.

The difference in intensity of two sides of some plates, particularly that of pilchard oil, is due to improper screening. The black spot, which overlaps the central spot made by the lead on the front of the plate holder, is caused by some experimental error which has not yet been found.

IV. CONCLUSION

The study of x-ray diffraction patterns has not progressed as rapidly as desired because of the long time necessary for exposure. Intensifying screens that have been used have not been satisfactory. A higher potential is the only other method of increasing the intensity.

Tentative arrangements have been made for the design of a cell which will allow substances to be examined over a temperature range -100° C to 400° C or higher. By studying the intensity of the diffraction patterns with a microphotometer, interesting results should be obtained. The temperatures at which the solid changes to liquid and the liquid to gas would be particularly important.
Benzene ($C_6H_6$)

Cyclohexane ($C_6H_{12}$)
Ethyl Alcohol \( (\text{C}_2\text{H}_5\text{O} \ \text{H}) \)

Ether \( (\text{C}_2\text{H}_5\text{O} - \text{C}_2\text{H}_5) \)
Acetic Acid \((\text{CH}_3\text{COO-H})\)

Ethyl Acetate \((\text{CH}_3\text{COO-CH}_2\text{CH}_3)\)
Ethyl Malonate  $\text{CH}_2\text{(COO-C}_2\text{H}_5\text{)}_2$

Pilchard Oil
BIBLIOGRAPHY


