X-RAY DIFFRACTION IN LIQUIDS

by

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C O N T E N T S

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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 R

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

$$I = C \, exp \left\{ - \frac{1}{16} \frac{N}{RT\beta} l_0^3 \left(1 - \frac{\sin^3 \theta_1}{\sin^3 \theta_0} \right)^2 \right\}$$

where l_0 is the mean distance between neighboring molecules and given by Bragg's equation $\lambda = 2 l_0 \sin \theta$, β is the isothermal compressibility of the fluid, θ_0 is the half diffraction angle for the principal halo, and θ_1 for any scattering angle.

If I is plotted against $\frac{\theta_1}{\theta_0}$ the sharpness of the maximum depends upon $\frac{l_0^3}{\beta}$. 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

3.

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 anyother 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.   T he 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 moleculess 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.

4. Zernike and Prins Theory.

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
agrément 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 30,000 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.

0 - 1	Resistance	·	0.231 ohms.
0 - 2	"		0.242 "
0 - 3	"		0.255 "

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 wave-
length 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
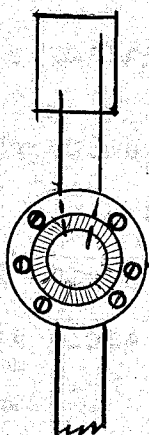cooled by convection in a long, insulated brass vessel
filled with water.

The x-ray tube is evacuated by means of a
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 milliameter.

3. Spectrograph and Cell.

The Dr. Müller x-ray spectograph 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 to-
gether 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 clamp-
ing 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 30 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 $\overset{H}{\underset{C}{\diagdown}}C\overset{H}{\underset{C}{\diagup}}$ seems to be much more effective in scattering x-rays than $\overset{H}{\underset{C}{\diagdown}}C = C.$ The change in intensity might be due to the addition of more hydrogen ($C_6 H_{12}$ as compared to $C_6 H_6$) 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 (80^0 C) so no difference in size or diffuseness of the ring would result in that case. Ether, however, boils at 35^0 C while alcohol boils at 78^0 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 tripple 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 wave-length 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.
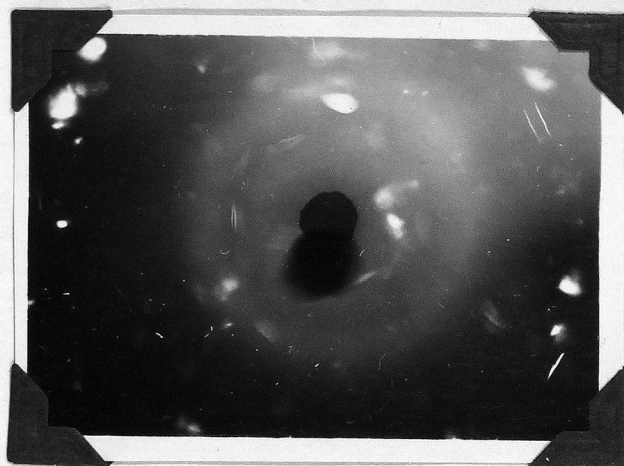
X-RAY DIFFRACTION PATTERNS
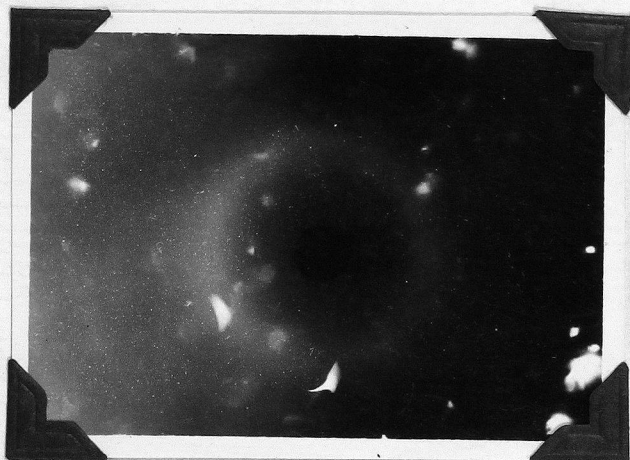
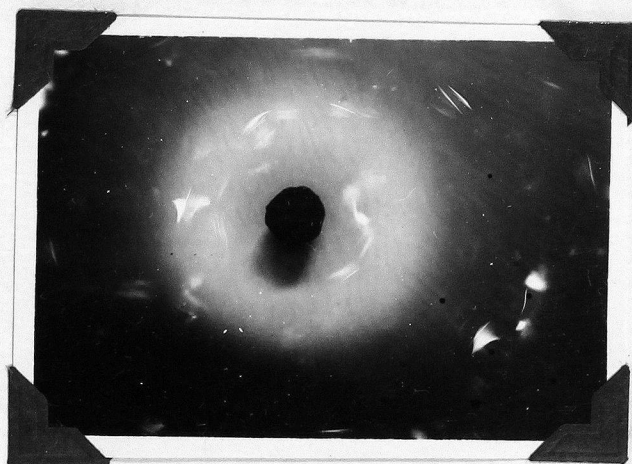Benzene $(C_6 H_6)$
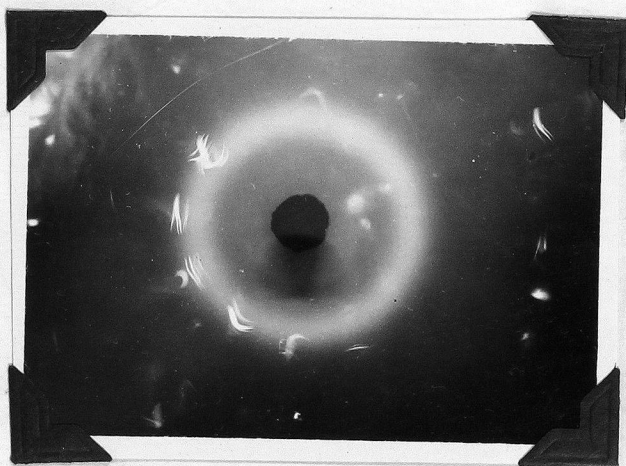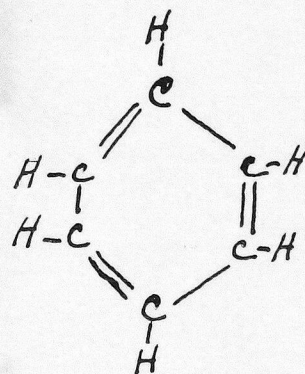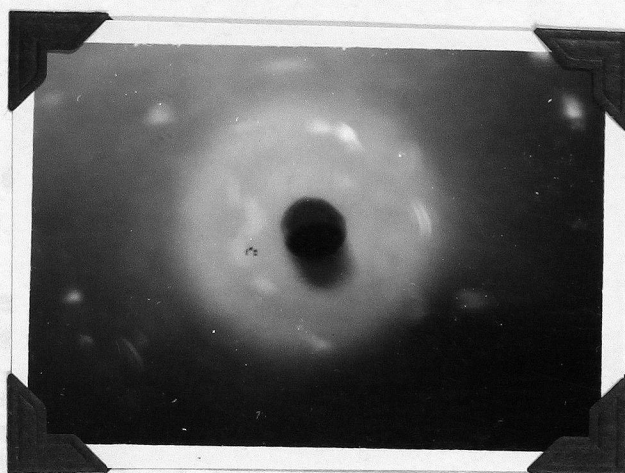

Cyclohexane $(C_6 H_{12})$
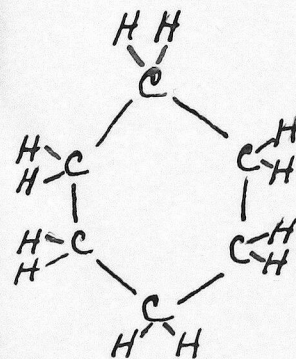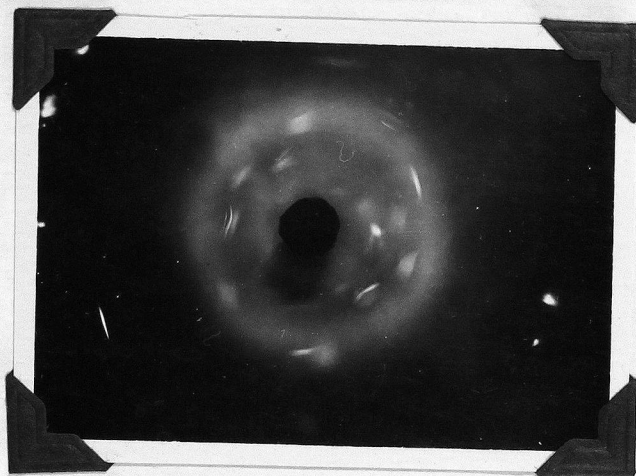
Ethyl Alcohol (C_2H_5O H)
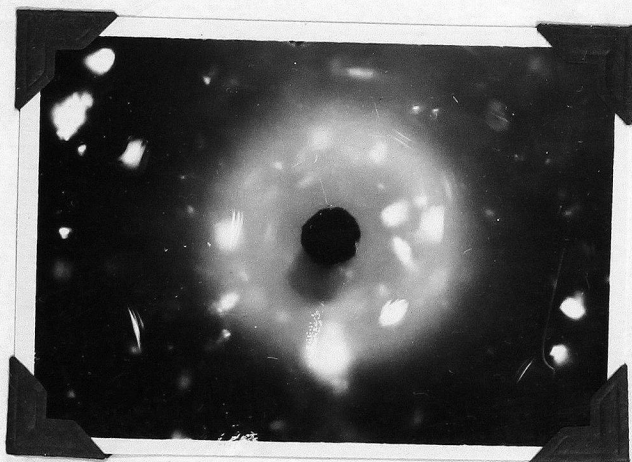
Ether (C_2H_5O-C_2H_5)

Acetic Acid (CH$_3$COO-H)

Ethyl Acetate (CH$_3$COO-C$_2$H$_5$)

Ethyl Malonate $CH_2(COO-C_2H_5)_2$
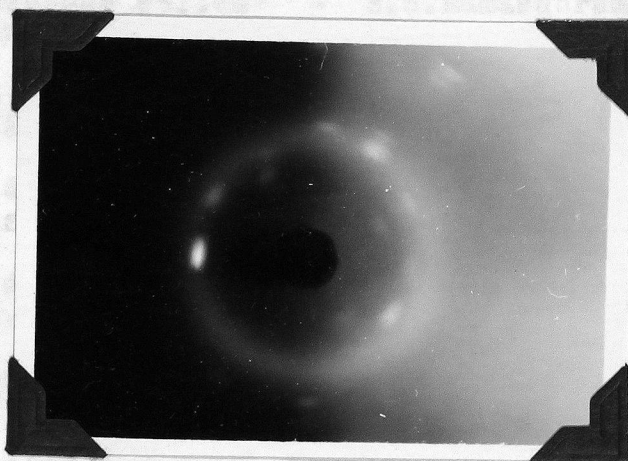
Pilchard Oil

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