Further Investigation of X-Ray Diffraction in Liquids, Part III. Influence of Temperature

By

Shinsuke Tanaka and **Akira Tsuji**

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Abstract

The influence of temperature on the X-ray diffraction in seven liquids were studied by the photographic method. The camera with a long narrow slit was attached by the heating and cooling device specially designed. Four effects were commonly recognised, though they were characteristic for each liquid; i. e. (1) contraction of the position of the diffraction band, (2) broadening of the band and diffuseness of edges, (3) increase in the inner scattering, (4) decrease in the intensity of the diffracted X-rays.

Experimental Part

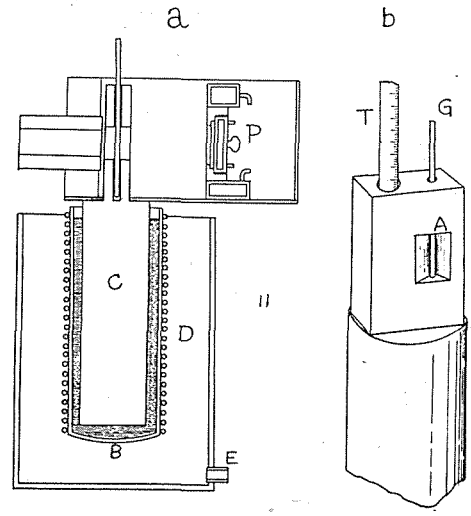
The apparatus for generating X-rays was the same as used in the previous experiment, while the photographic camera was attached by the heating and cooling device specially designed. The Shearer metal tube, having a copper anticathode, was evacuated by a molecular pump and excited by a transformer at about 50 kilovolts. The current through the tube was 4-5 milliamperes and the time of exposure 4-5.5 hours according to the temperature of the samples. A rectangular hole was perforated in the bottom of the photographic camera, through which a copper rod carrying the specimen was inserted. The lower part of the rod was heated by an electric furnace or cooled by the freezing mixture. This device is represented in Figs. 1 a and 1 b. Fig. 1 a shows the total cross-section and Fig. 1 b the appearance of the upper part of the rod.

The upper part of a circular rod of diameter 3cms. and length

15cms. was cut off into a rectangular form 4.5cms. in height and 1cm. in breadth. Two circular holes were bored vertically into this rectangular part, one having a thermometer and the other the glass tube containing the sample. A small aperture 1.5cms. long and 1.5mm. broad was perforated parallel to the latter hole in order to pass the X-ray beam and cause it to impinge upon the sample. The back part of the slit was opened to facilitate the passage of the diffracted X-rays. T,G and A in Fig. 1 b are the thermometer, the glass tube and the aperture respectively.

The rectangular part of the rod is inserted into the camera as shown in Fig. 1 a and the aperture is placed just behind the slit, 0.4 mm. in breadth and 1.5cms. in length, in the camera. The lower part of the rod C is placed in the porcelain tube B, which is filled up with glycerin and coiled round with nichrome wire. The porcelain tube is placed in a large vessel D. High temperatures are obtained by passing an electric current through the nichrome wire and low temperatures, by filling up the vessel D with freezing mixture. E is the outlet for water. Water was constantly circulated through the plate holder represented by P, during the exposure in order to keep the plate at constant temperature. With this device, the temperature of the rod could be changed from −10° to 300°C and the limit of the variation during the exposure could be kept under three degrees.

Fig. 1



The long thin glass tube of elliptical cross section was sealed after the sample had been put in, so that the liquid could not boil on account of increase in the vapour pressure until the glass tube was broken. When we want to raise the temperature as high as possible, we must use a thick glass tube, which produces a harmful confusion on the photographic plate by its own diffraction of X-rays. Many photographs were at first taken with an empty glass tube in order to minimize

this trouble as much as possible. The direct beam was also cut off by a thin lead plate to avert its bad effects. The photographs are reproduced in the annexed plate.

The distance between the sample and the photographic plate was 4.06cms. and the following seven liquids were examined at various temperature; pyridine[M], pyrrol[T], cyclohexane[T], nitrobenzene[K], heptane[K], heptyl alcohol[M], oleic acid[K]. The former four liquids belong to the cyclic compounds and the latter three to the chain compounds. These liquids were considered to be typical ones from the previous experiment. The letters M, K and T, attached to the names of the samples indicate Merk, Kahlbaum and Takeda (Japan), the manufacturers.

Results and Discussion

The influence of temperature on the X-ray diffraction in liquids was investigated by Raman[1], Ramasubramanyan[2], and Vaidyanathan[3]. The second author took liquids which indicated only one intensity maximum in the diffraction photographs and the third took ones indicating two maxima. They found, in general, the following effects: (1) A visible contraction of the radius of the diffraction ring due to the thermal expansion of liquids, (2) Broadening of the ring and diffuseness of the edges due to the increased displacement of molecules from their mean positions, (3) Large amount of inner scattering due to the local fluctuations of density of scattering electrons, (4) For the haloes having two intensity maxima the inner one becomes diffuse more quickly than the outer one.

The present authors took many photographs at various temperatures with the samples previously mentioned and observed more precisely the above effects. The photographs taken with a narrow long slit show their characteristics more clearly than those taken with a pin hole. In addition to the above effects the authors recognised decrease in the intensity of the diffracted X-rays at the higher temperatures. Moreover each liquid exhibited these effects in a different manner. A brief description is written below.

1. Contraction of the position of the diffraction bands :— The spacings corresponding to the intensity maxima were calculated

1. Nature, **120**, 770 (1927)
2. Ind. Jour. Phys., **3**, 137 (1928)
3. Ind. Jour. Phys., **3**, 391 (1929)

by Bragg's equation and are given in the following Table I. In some cases the temperature rose higher than the boiling point at the normal pressure, but the liquid did not boil on account of the increase in the vapour pressure. The boiling and melting points in the table relate to the normal pressure except in the case of oleic acid, and are obtained from Landolt and Börnstein's physico-chemical tables. d_1 and

Table I

Name of liquid	Temperature	Spacings (A. U.) d_1	d_2	$\sqrt[3]{\frac{m}{\rho}}$ (A. U.)
Pyridine	−10°	4.91	—	4.94
M. p. −42°	52°	5.10	very faint	5.17
B. p. 115°.5	111°	5.21	very faint	5.27
	162°	5.33	—	5.34
Pyrrol	−10°	4.72	—	
B. p. 131°	54°	4.81	very faint	
	106°	4.95	—	
	158°	5.06	—	
Cyclohexane	7°	5 29	very faint	
M. p. 6°.5	80°	5.46	very faint	
B. p. 181°.4	133°	5.56	very faint	
Nitrobenzene	9°	6.10	3.71	
M. p. 8°.7	112°	7.47	3.91	
B. p. 210°.8	200°	very diffuse		
Heptane	−9°	5.21	—	6.04
M. p. −90°	58°	5.51	—	6.19
B. p. 98°.4	110°	5.65	very faint	6.32
	162°	5.85	—	6.41
Heptyl alcohol	−9°	4.72	10.00	6.13
M. p. −34°.6	58°	4.89	11.42	6.24
B. p. 175°.8	125°	5.06	faint	6.36
	181°	5.38	very faint	6.45
Oleic acid	19°	4.81	10.19	
M. p. 19°	71°	4.91	12.09	
B. p. 286°	123°	5.14	12.56	
	175°	5.21	faint	
	225°	5.38	faint	

d_2 represent the spacings corresponding to the outer and the inner maximum respectively, m the mass of one molecule, and ρ the density

at each temperature, obtained by neglecting the volume change due to the increase in the pressure.

The inner maximum was found for heptyl alcohol and oleic acid at a comparatively low temperature, as in the case of the previous experiment, and it became too faint for its exact position to be ascertained at higher temperatures. Other liquids for which we could not find the inner maximum in the previous experiment, indicated a very faint inner maximum in some temperature range though the exact position could not be determined. The increase in the spacing for the principal maximum is not parallel to the rise of the temperature and it is always smaller than that for the inner maximum, as shown in Table I. The change for the chain compounds, however, is somewhat greater than that for the cyclic compounds. The nitrobenzene band, which is very diffuse at ordinary temperatures, becomes more and more diffuse as the temperature increases and finally it comes to have nearly an uniform blackening, and two values of d_1 corresponding to the inner and the outer limits of the band could not be obtained.

The increase in the spacing can be simply explained qualitatively by the expansion of the liquid, but the quantitative increase seems to be greater than that expansion. Further investigations is necessary to obtain a more precise interpretation.

2. *Broadening of the diffraction bands*:—The broadening of the diffraction bands and the diffuseness of their edges were generally caused by the increasing of the temperature though they are not proportional. As the influence is also characteristic for each liquid, it will be briefly given below.

Pyridine: The photographs taken below 111°C show the gradual increase of the influence and at 162°C there is a rapid increase.

Pyrrol: The effect of broadening predominates between −10° and 54°C, and that of diffuseness between 106° and 158°C.

Cyclohexane: This gives a very sharp maximum which is little influenced by the temperature. A very faint inner maximum is found at 7°C.

Heptane: The influence is slight, but proportional to the increasing temperature.

Heptyl alcohol: A great influence upon the outer maximum is observed and especially at 181°C. The increase in the inner scattering diminishes the relative intensity of the inner maximum which was, however, recognized up to 181°C.

Oleic acid : The influence upon the outer maximum is small but that upon the inner one resembles the case of heptyl alcohol.

Nitrobenzene : This gives a rather sharp maximum at 9°C and at the other temperatures a very broad and diffuse band.

These influences may be naturally explained by the thermal agitation of the molecules in liquids though there can not be found any simple relationship to the assumed molecular form. It is interesting to note that an inner maximum can be found in some temperature range. This seems to indicate that the association of molecules predominates at this temperature.

3. Increase in the amount of the inner scattering :—The scattering inside the principal maximum increases remarkably in a different manner for each liquid, though there can not be found any relationship to the assumed forms of the molecules. The origin of this influence is probably somewhat complex and more investigations are necessary.

Pyridine : The inner scattering on the photograph taken at 162°C is particularly great, and those corresponding to −10°, 52°, 111°C show only a gradual increase.

Pyrrol, Heptane and *Oleic acid :* These liquids show a gradual increase in inner scattering as the temperature increases.

Cyclohexane : The influence of temperature is again very small in spite of the scattering being comparatively large at ordinary temperatures.

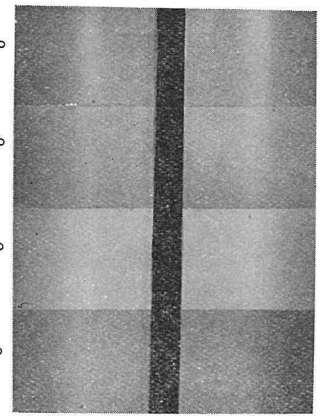
Nitrobenzene : The broadening of the bands is so great that the inner scattering can scarcely be distinguished from it at higher temperatures.

Heptyl alcohol : Of the four photographs, two corresponding to the lower temperatures show equally smaller inner scattering than the other two, which have nearly equal intensity.

4. Decrease in the intensity :—When we take the photographs at higher temperatures, we need a longer time of exposure in order to get equally good intensity. This is probably due to the effects above mentioned and consequently cyclohexane is an exceptional case.

Physical Laboratory,
The Osaka University of Engineering,
June 10, 1930.

Pyridine



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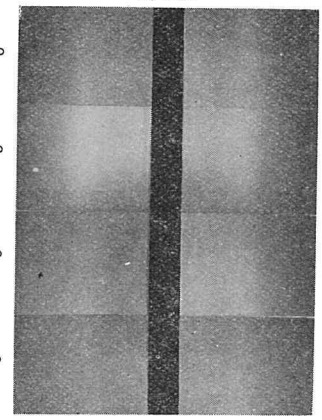
Pyrrol



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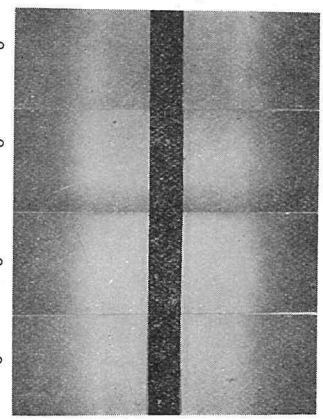
Normal Heptane



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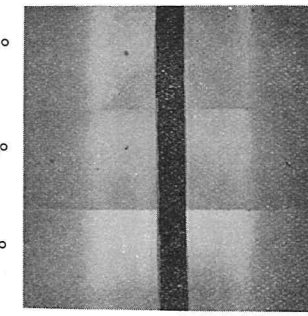
Cyclohexane



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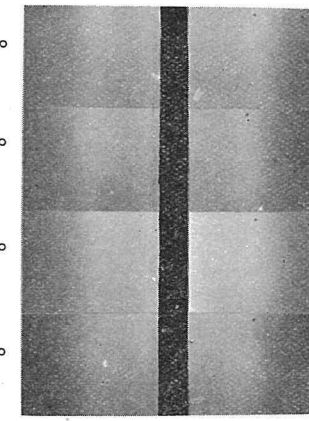
Normal Heptyl Alcohol



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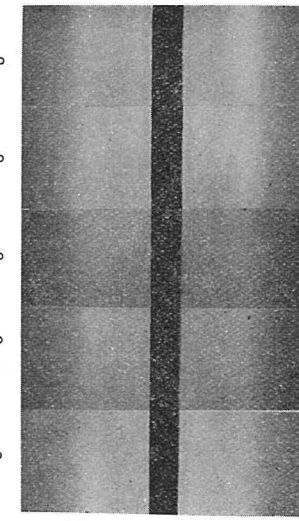
Oleic acid



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