Further Investigation of X-Ray Diffraction in Liquids, Part I. Aqueous and Non-aqueous Solution

By

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Abstract

X-ray diffraction in aqueous and non-aqueous solutions of several substances has been studied by using the Cu K radiation. In the case of the aqueous solutions, the results seem to agree with the recent investigations of P. Krishnamurti though our photographs are not so good. In the case of some non-aqueous solutions, however, quite different phenomena are observed. Dilute aqueous solutions give a pattern consisting of the outer ring due to the water, and a corona around the central spot. With increasing concentration the intensity of the corona increases gradually and finally it develops into a halo. Dilute non-aqueous solutions—benzene, ethyl ether and ethyl alcohol are the solvents—give only a fine ring of somewhat smaller diameter. With increasing concentration the diameter of the ring decreases markedly, and the inner scattering does not increase; the outer scattering, on the contrary, increases gradually, and finally it develops, in some cases, into a halo of large diameter. The solutions of camphor in benzene show it most clearly.

When the authors studied the X-ray diffraction in various kinds of organic liquids, they also investigated that in several mixtures[1] of those liquids, and found that the halo of the mixture did not show superposition of the haloes of each of the components but indicated an other characteristic figure. This seemed to indicate that the halo was due to diffraction by neighbouring molecules i. e. the cause of the halo was intermolecular and not intramolecular.

In the present experiment the X-ray diffraction in aqueous and non-aqueous solutions of several substances was studied by using the

1 These Memoirs, **13**, 1 and 17. (1930)

Cu K radiation. The apparatus and the conditions of the experiment were the same as in the previous ones except that the current in the tube was now about 5 milliamperes and hence the time of exposure about 2 hours.

For the aqueous solutions, cane sugar, citric acid, ammonium nitrate, potassium hydroxide, and sodium chloride manufactured by Merk were taken as the solutes, the former two being non or weak electrolytes and the latter three strong electrolytes. The photographs were taken for several concentrations with each solute, and seemed to indicate generally the same results as those of the recent investigations of P. Krishnamurti[1], though our photographs were not so good. Dilute solutions give a pattern consisting of the outer ring due to the water, and a corona around the central spot. With increasing concentration the intensity of the corona increases gradually and finally it develops into a halo. The size and the intensity distribution of the halo showed a gradual change in accordance with the concentration as well as with its own increasing diffuseness and lack of clearness, and the maximum sharpness of the halo was given with the solutions in which the solute and the solvent were nearly equal. The haloes were, unfortunately, too diffuse for their characteristic appearance to be observed more precisely, and hence our considerations could not be developed. It may, however, be concluded that the increased inner scattering is caused by the irregularly distributed molecules of the solute and that the outer ring is originated by the neighbouring molecules of two kinds (solute and solvent), and hence the origin of the halo is probably again intermolecular.

From the point of view of the diffuseness of halo, water is not a suitable solvent for our purposes, and consequently organic solvents like benzene, ethyl ether and ethyl alcohol which give a sharper and clearer halo in the pure state are taken for the solvents. All the samples used except the camphor, which is made in our country, were manufactured by Merk. Some of the photographs obtained with the organic solutions and the powder photograph of camphor are reproduced in Plates I and II.

(1) Benzene and Camphor

Benzene gives a very fine and intense halo accompanied by a

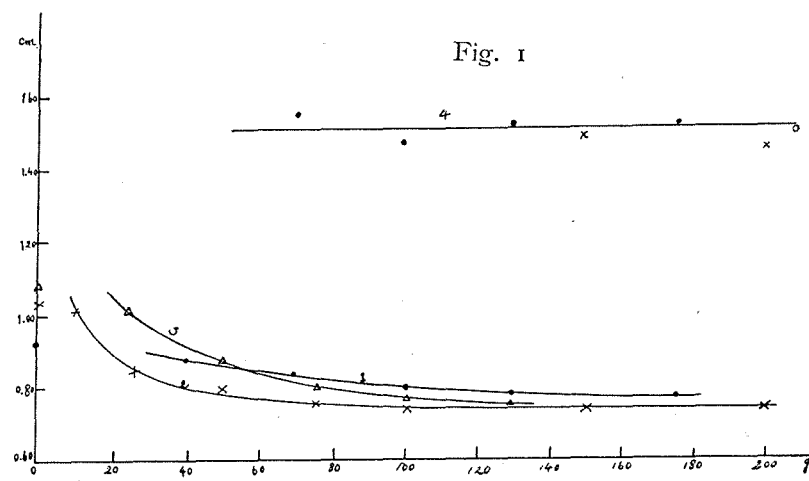
1 Krishnamurti; Ind. Jour. Phys. **2**, 501 and **3**, 209, (1928)

feeble but distinct scattering outside of it. Inner scattering is comparatively small. The X-ray powder photograph of Debye and Scherrer for camphor shows two broad and strong rings. The haloes of the dilute solutions are similar to that of benzene only and the marked increase of the inner scattering cannot be observed as in the case of the aqueous solutions. With increasing concentration, the outer scattering, on the contrary, increases gradually until it comes to have a maximum at the position where the outer ring in the powder photograph of camphor will appear. This outer maximum is observable with solutions having a concentration of over 100 : 70 by weight, and for a good ring the most concentrated solution is 100 : 176 by weight. The outer scattering, however, is considerable but uniform at the concentration of 100 : 40 and it becomes more feeble and diffuse with decreasing concentration. Unlike the outer scattering, which attains a maximum of intensity with concentrated solutions, the principal halo with dilute ones becomes more and more diffuse. It is interesting to note that the radius of the position of the outer maxi-

Table 1

Concentration (by weight)		Inner ring		Outer ring	
Benzene	Camphor	Radius	Spacing	Radius	Spacing
100	0	0.92cm	5.06A.U.	— cm	— A.U.
100	40	0.88	5.28	—	—
100	70	0.84	5.51	1.55	3.18
100	100	0.81	5.70	1.46	3.33
100	130	0.79	5.80	1.51	3.23
100	176	0.78	5.87	1.51	3.23
0	100	0.80	5.74	1.49	3.31

Fig. 1



mum is just the same as that of the outer ring of the powder photograph of camphor, and is independent of the concentration; the size of the principal halo, however, decreases markedly with increasing concentration. The rate of the contraction of the principal halo is greater for dilute solutions; it is denoted by curve 1. in Fig. I. The weights of camphor in 100gr. solvents are represented in abscissa and the radii for corresponding haloes in ordinate. In Fig. I, curve 4 denotes the radii of the outer maximum obtained with the various solutions and camphor only. The mark o represents the radius of the outer ring of camphor and the mark • those of the present solutions. The radii and the spacing calculated by Bragg's equation are writen in the Table 1. The wave length of the X-ray is taken as 1.54 A.U.

(2) Ethyl Ether and Camphor

The ethyl ether halo is more or less diffuse compared with the benzene halo, and the inner scattering is rather intense especially near the direct spot. For concentrated solutions of the compositions 100 : 200 or 100 : 150 by weight, the outer maximum can be easily observed though it is fainter than in the case of the benzene solutions. The solutions of less concentration show haloes having only the uniform outer scattering, which seems to decrease rapidly at the concentration of about 100 : 100 by weight. The increase of the inner scattering by the dissolving of the camphor is not again recognized, and the principal halo shows its maximum sharpness at the concentration of about 100 : 100 though it is more diffuse than the halo of pure ether.

The size of the outer maximum is constant for all concentrations and equal to that of the benzene solution. The principal halo, however, contracts gradually with increasing concentration through the comparatively dilute solutions, until it reaches nearly a constant at concentrations of over 100 : 100 by weight. This is shown by curves 4 and 2 in Fig. I. The mark × in curve 4 denotes the observed values of the radii for the present solutions.

The radii and the spacings corresponding to the various concentrations are also tabulated in Table 2.

(3) Ethyl Alcohol and Camphor

The ethyl alcohol halo has a considerable inner scattering which shows an intense maximum near the central spot, and thus it looks

Table 2

Concentration (by weight)		Inner ring		Outer ring	
Ethyl ether	Camphor	Radius	Spacing	Radius	Spacing
100	0	1.03cm	4.53A.U.	— cm	— A.U.
100	10	1.01	4.64	—	—
100	25	0 85	5.46	—	—
100	50	0.80	5.74	—	—
100	75	0.77	5.94	—	—
100	100	0.75	6.12	—	—
100	150	0.75	6.12	1.48	3.30
100	200	0 75	6.12	1.44	3.38
0	100	0.80	5.74	1.49	3.31

as if it were composed of two rings. This inner maximum becomes less intense on the camphor being dissolved and immediately disappears with increasing concentration. Although the outer scattering increases gradually, the ring of the outer maximum intensity does not appear even with the most concentrated solution (100 : 130 by weight). The principal halo, however, shows the same change as in the case of the former solutions; i. e. its size contracts with increasing concentration until it reaches a constant value, and its sharpness is best with the solution of the concentration of 100 : 100 by weight. The radii and the spacing for solutions of various concentrations are tabulated in Table 3, and their change with the concentrations is represented by curve 3 in Fig. I.

It is interesting to note that the sizes of the haloes with the most concentrated solutions for each solvent are nearly equal even though the haloes of all the solvents show different values.

Table 3

Concentration (by weight)		Inner ring		Outer ring		Inner max. for alcohol	
Ethyl alcohol	Comphor	Radius	Spacing	Radius	Spacing	Radius	Spacing
100	0	1.07cm	4.43 A.U.	— cm	—A.U.	0.57cm	7.94 A.U.
100	25	1.01	4.64	—	—	—	—
100	50	0.88	5.28	—	—	—	—
100	75	0.81	5.75	—	—	—	—
100	100	0.78	5.87	—	—	—	—
100	130	0.75	6.12	—	—	—	—
0	100	0.80	5.74	1.49	3.31	—	—

(4) Ethyl Alcohol and Resorcinol

Resorcinol is also a cyclic compound having a simple molecular constitution. In this case, the outer scattering increases very slightly compared with that obtained with the camphor solution, and hence the outer ring characteristic of the solute does not appear even with the most concentrated solution, 100 : 130 by weight. The contraction of the principal halo is now very small; the inner scattering, however, decreases gradually, and at some concentrations the inner maximum near the central spot, characteristic of pure alcohol, disappears and becomes an uniform blackening. Generally speaking, the principal halo becomes more or less diffuse again on the solute being dissolved and the maximum sharpness is obtained with the solution of the concentration of 100 : 100 by weight. The radii of the haloes and the corresponding spacings are given in Table 4.

Table 4

Concentration (by weight)		Inner ring		Inner max. for alcohol	
Ethyl alcohol	Resorcinol	Radius	Spacing	Radius	Spacing
100	0	1.07cm	4.43A.U.	0.57cm	7.94A.U.
100	50	1.09	4.30	0.55	8.03
100	100	1.06	4.43	0.50	9.06
100	130	1.04	4.51	—	—

(5) Benzene and Benzophenone, Naphthalene, Anthracene

In these cases the solvent and the solutes are all cyclic compounds like benzene and camphor. The molecular constitutions are rather complex and seem likely to give an outer ring owing to the intramolecular effect of the solutes. Their solubility, however, is unfortunately so small that the outer scattering no more longer shows the marked increase and does not give the outer ring of the maximum intensity. The solubility of benzophenone is greatest and hence the outer blackening is greatest. The contraction and the diffusing effect due to the solute are always easily observable. There is also no increase of the inner scattering even with dilute solutions. The radii of the haloes and the corresponding spacings for the

Table 5

Concentration (by weight)			
Bezene	Benzophenon	Radius	Spacing
100	0	0.92cm	5.06A.U.
100	50	0.96	4.84
100	70	0.93	4.96

solutions of benzophenone are given in the Table 5.

In conclusion the writers wish to express their hearty thanks to Prof. Ishino for the interest he has taken in the research.

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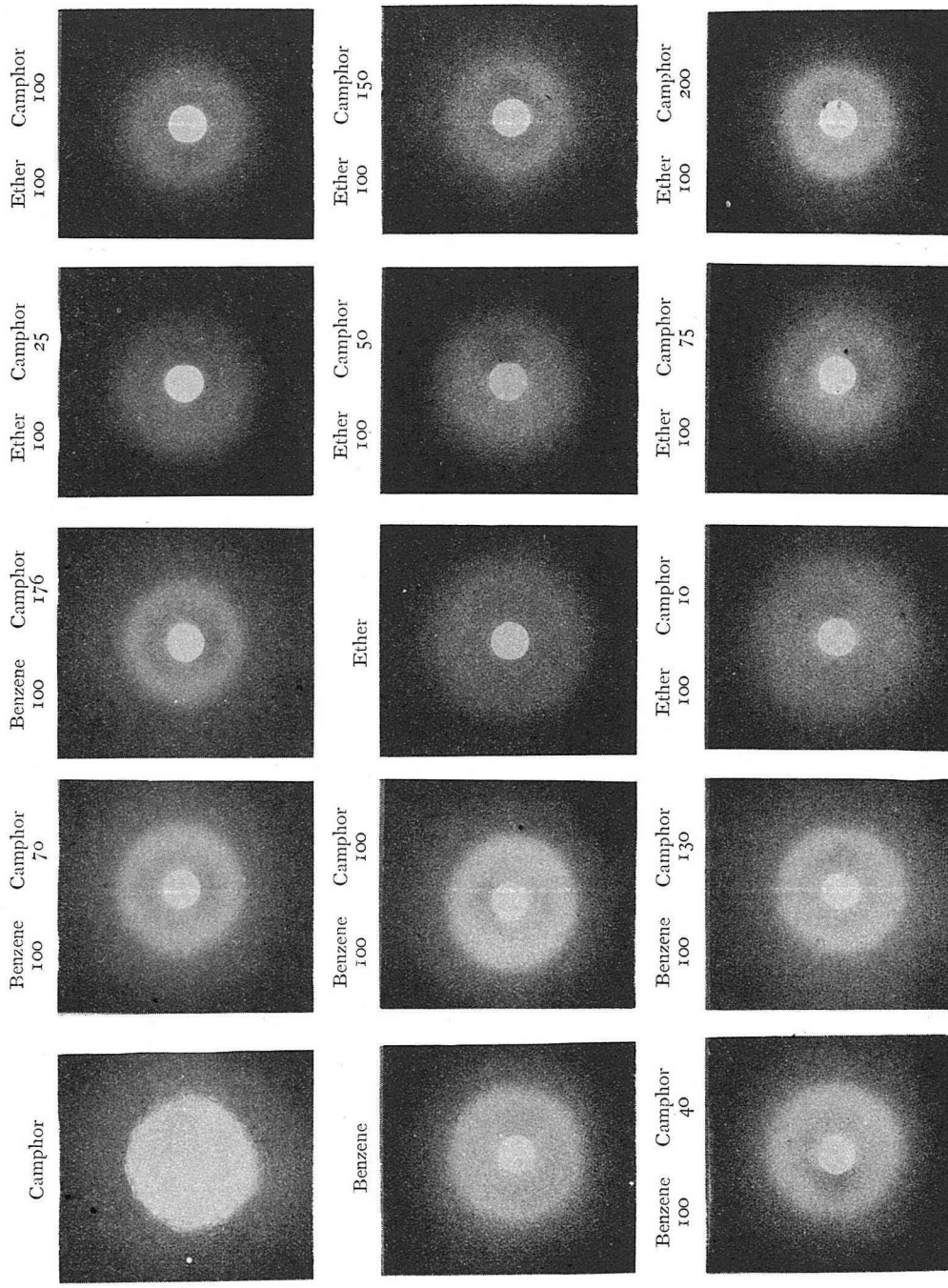
Plate. I


Camphor
Benzene 100 Camphor 70
Benzene 100 Camphor 176
Ether 100 Camphor 25
Ether 100 Camphor 100
Benzene
Benzene 100 Camphor 100
Ether
Ether 100 Camphor 50
Ether 100 Camphor 150
Benzene 100 Camphor 40
Benzene 100 Camphor 130
Ether 100 Camphor 10
Ether 100 Camphor 75
Ether 100 Camphor 200