

Studies on X-Ray Diffraction in Organic Liquids Part II. Chain Compounds

By

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Abstract

This is a continuation of the previous work. Thirty liquids of organic chain compounds were now investigated by the aid of the same apparatus. The diffraction haloes of four liquid paraffins show a single maximum intensity of nearly equal size, and those of the other liquids, two maxima of different intensities characteristic of the compounds. The size of the outer maximum is approximately constant and that of the inner maximum depends upon the number of carbon atoms in the molecule. The sizes and the intensity distributions in the haloes of iso-compounds are slightly different from the corresponding normal compounds. The unsaturated compounds show more diffuse and less clear maxima in their haloes than the saturated ones. The appearance of each figure is roughly described and the length of each molecule is computed by making some assumptions. Some of the results are those naturally expected from the chemical constitutional formulae, the others, however, are not.

Experimental Part

The same apparatus as was used in the previous experiment¹ was employed under the same conditions to take the photographs of X-ray diffraction haloes. The only difference was in the diameter of the circular slits, which was now about 1 mm. All the samples examined were chosen from the aliphatic compounds of organic liquids at the room temperature of about 10°C; those marked × and * in the following table were of Kahlbaum's and Merk's manufacture respectively, and the others were supplied by the Research Laboratory of Organic Chemistry of our College. All the photographs are reproduced in Plates I and II respectively.

¹ These Memoirs. 13. I (1930).

Appearance of Figures

The majority of the samples examined in our experiment were recently investigated by Sogani,¹ Stewart, Morrow, and Skinner². The former employed the photographic method and the latter the ionization method. The investigation, however, has been carried out from a different standpoint, and the observed facts do not coincide in some points. Stewart, Morrow and Skinner observed the two maxima in their intensity curves for all cases excepting the various paraffins, while Sogani found only one maximum in all his photographs. Our photographs clearly show two maxima of intensity for all the samples except the paraffin group, which show the same result as that obtained by the former investigators. In their intensity curves, however, the inner maximum is always very small compared with the outer one, while in our photographs, the relative intensities of the two maxima show quite different values characteristic of each sample, as described below. The spacings d corresponding to the maximum intensity of all the paraffin haloes and those for the outer maximum of haloes of other compounds are approximately constant independent of the carbon content of the molecules, and on the other hand those corresponding to the inner maximum depend upon the number of carbon atoms in the molecules, as noted by Stewart and Morrow.

The value of the increase per carbon atom, however, is somewhat smaller than that obtained by the above authors. These are given in the fifth column of Table I. A rough idea of the distribution of intensity in the haloes will be obtained from the curves given in the third column of the same table. Now we shall describe the appearance of each figure.

1. *Paraffin*

In these compounds normal pentane, normal hexane, normal heptane and amylene are examined. All the haloes of the former three compounds show a single sharp maximum of about equal size accompanied by a small scattering outside of it. The inner scattering is also small and it is very difficult to distinguish the one from the other.

¹ Sogani: *Indian Jour. Phys.* **2**, 97 (1927).

² Stewart and Morrow: *Phys. Rev.* **30**, 232 (1927).

Stewart and Skinner: *Phys. Rev.* **31**, 1 (1925).

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

Stewart: *Phys. Rev.* **31**, 174 (1928) and 32, 153 (1928).

An amylene molecule has five carbon atoms like pentane, but ten hydrogen atoms instead of twelve. The halo shows a marked scattering on both sides of the maximum intensity, which is slightly smaller than the pentane halo. The inside scattering is greater than the outside. This difference in the figures obtained from saturated normal paraffins must be caused by a double bond which will make the molecule more unsymmetrical.

2. Alcohol

Methyl alcohol: — Of the two intensity maxima the outer one is more or less stronger than the inner one, and the scattering between them is remarkable. The small angle scattering is very little and the outside scattering is also small.

Ethyl alcohol: — The intensities of two maxima are nearly equal. The scattering between two maxima is small, and the outside one is also small but the inside scattering is so great that the distinction between it and the inner maximum is scarcely observable.

Normal and Iso-propyl alcohol: — The outer maximum of *n*-propyl alcohol halo is very fine on account of the smallness of the scattering on both sides of it, and its intensity is much greater than that of the inner one. The central scattering is somewhat marked. The intensity of the outer maximum of iso-propyl alcohol is, on the contrary, so weak compared with the comparatively large inside scattering that its position can hardly be noticed. The intensity of the inner maxima is slightly stronger than that of the outer in spite of the great scattering on both sides. The size of the outer maximum of the former is greater than that of the latter, but the contrary is the case with the size of the inner maxima. If we take the spacings for two maxima calculated by Bragg's formula as the diameters and lengths of the molecules, the above fact will be naturally explained from the chemical constitutional formulae.

Normal and Iso-butyl alcohol: — The normal butyl alcohol halo has a strong fine outer maximum and a weak inner maximum like the *n*-propyl alcohol halo. The scattering of the other parts is, however, somewhat greater than that of the latter. The iso-butyl alcohol halo shows two indistinct maxima on account of greater scattering in the other parts, like the iso-propyl alcohol halo. The intensity of the outer maximum is, in this case, greater than that of the inner one. It must be noticed that the relation between the sizes of the maxima of two

haloes is quite similar to the case of propyl alcohol, as is seen in Table I.

Iso-amyl alcohol:— Even though this halo gives two comparatively sharp maxima, it still shows the characteristic appearance of the iso-alcohol halo by the indistinctness of its intensity and its size. The outer maximum is much greater than the inner, as in the case of iso-butyl alcohol.

Normal hexyl and normal heptyl alcohol:— These alcohols give a halo which has a sharp strong outer maximum. It is unfortunately very difficult to ascertain the position of the inner maximum owing to the great central scattering and its small size. The outer limit of the inner maximum is, however, quite sharp.

Allyl alcohol:— This molecule has the same number of carbon atoms as the propyl alcohol one, notwithstanding the lack of two hydrogen atoms. There is a considerable scattering outside the outer maximum, which makes it diffuse. The inner maximum is too faint to be discriminated from the central scattering. The sizes of the two maxima are just between those of normal and iso-propyl alcohol. This can be understood from the constitutional formulae. This difference in appearance seems to be common to that between the pentane and the amylene halo.

Geraniol:— There is only one maximum accompanied by a marked scattering on both sides of it. The inner maximum has probably vanished owing to the smallness of its size, which might be easily accounted for by the large content of carbon atoms in the molecule.

Ethylene Glycol and Glycerine:— There are two maxima of nearly equal intensity. The scattering of the other parts is comparatively great. The size of the halo of the former liquid is slightly greater than that of the latter's, which might be expected from the knowledge of the constitutional formulae, but they do not show such a great difference from the corresponding normal alcohol halo as expected from the constitutional formulae. This may be a case where the chemical formula does not give an idea of the real molecular form.

3. Acid

Formic acid:— Two maxima are clearly observable in spite of the great scattering in the other parts. The outer maximum is a little weaker than the inner. It is interesting that there is a space around the direct spot where the scattering is extraordinarily small. The halo

Table I

Name of Liquid	Rational Formula	Appearance	Angle of Diffraction		Spacing (A.U.) $d_{obs.}$		Density ρ	Spacing (A. $d_{calc.}$	
			θ_1	θ_2	d_1	d_2		d_2'	a
Formic acid*	H COOH		24° 8'	13° 36'	3.68	6.52	1.224(20°)	4.62	5
Acetic acid*	CH ₃ COOH		21° 57'	11° 29'	4.03	7.70	1.05 (20°)	5.85	6
Propionic acid*	CH ₃ CH ₂ COOH		19° 11'	10° 22'	4.64	8.56	0.995(20°)	5.75	6
Normal butyric acid	CH ₃ (CH ₂) ₂ COOH		20° 37'	9° 46'	4.30	9.06	0.960(18°)	8.25	9
iso butyric acid	(CH ₃) ₂ CH COOH		18° 31'	10° 22'	4.78	8.56	0.950(19°)	6.75	7
iso valeric acid*	(CH ₃) ₂ CHCH ₂ COOH		16° 33'	8° 25'	5.35	10.55	0.956(20°)	6.21	7
Normal caproic acid*	CH ₃ (CH ₂) ₄ COOH		19° 2'	8° 15'	4.66	10.69	0.922(20°)	9.66	11
Caproic acid*	CH ₃ CH OH COOH		18° 22'	10° 22'	4.84	8.56	1.248(15°)	5.12	5
Sebacic acid*	C ₈ H ₁₇ CH : CH(CH ₂) ₇ COOH		18° 31'	9° 36'	4.78	9.17	0.891(12°)	23.06	26
Ethyl alcohol*	CH ₃ OH		22° 18'	11° 29'	3.99	7.70	0.796(15°)	4.20	4
Propyl alcohol*	C ₂ H ₅ OH		20° 25'	11° 9'	4.35	7.94	0.794(15°)	5.09	5
Normal propyl alcohol	CH ₃ CH ₂ CH ₂ OH		18° 53'	9° 26'	4.70	9.39	0.804(20°)	5.56	6
iso propyl alcohol*	(CH ₃) ₂ CH OH		17° 17'	10° 9'	5.12	8.75	0.789(20°)	4.83	5
Normal butyl alcohol*	CH ₃ (CH ₂) ₂ CH ₂ OH		18° 31'	9° 2'	4.78	9.76	0.810(20°)	6.66	7
iso butyl alcohol*	(CH ₃) ₂ CH CH ₂ OH		17° 4'	9° 36'	5.20	9.17	0.800(18°)	5.70	6
Normal amyl alcohol*	(CH ₃) ₂ CH (CH ₂) ₂ OH		17° 57'	9° 12'	4.94	9.63	0.810(20°)	7.41	8
Normal hexyl alcohol*	CH ₃ (CH ₂) ₄ CH ₂ OH		18° 22'	8° 25'	4.84	10.55	0.821(20°)	8.83	10
Normal heptyl alcohol*	CH ₃ (CH ₂) ₅ CH ₂ OH		18° 41'	7° 56'	4.75	11.16	0.830(16°)	10.31	11
Octyl alcohol	CH ₂ : CH CH ₂ OH		19° 33'	9° 36'	4.53	9.17	0.858(15°)	5.48	6
Geraniol	C ₉ H ₁₅ CH ₂ OH		17° 17'	—	5.12	—	0.881(16°)	11.11	12
Ethylene glycol	CH ₂ OH CH ₂ OH		21° 16'	11° 19'	4.17	7.86	1.004(20°)	5.85	6
Glycerine	CH OH CH ₂ OH		20° 4'	10° 56'	4.43	8.11	1.260(20°)	6.15	7
Acetone*	CH ₃ COCH ₃		19° 11'	10° 22'	4.64	8.56	0.797(15°)	5.62	6
Acetaldehyde*	CH ₃ CHO		21° 49'	11° 29'	4.07	7.70	0.788(16°)	5.61	6
Dimethyl ether	C ₂ H ₅ OC ₂ H ₅		19° 42'	9° 59'	4.51	8.85	0.718(17°)	8.43	9
Formaldehyde*	(CH ₂ HCO) ₃		22° 18'	9° 36'	3.99	9.17	0.994(20°)	13.88	16
Paraffin nylene*	CH ₂ : CH (CH ₂) ₂ CH ₃		17° 4'	—	5.20	—	—	—	—
Normal pentane*	CH ₃ (CH ₂) ₃ CH ₃		17° 48'	—	4.96	—	0.659(11°)	7.40	8
Normal hexane*	CH ₃ (CH ₂) ₄ CH ₃		17° 48'	—	4.96	—	0.660(21°)	8.82	10
Normal heptane*	CH ₃ (CH ₂) ₅ CH ₃		17° 17'	—	5.12	—	0.733(18°)	8.67	10

is larger than any of the others.

Acetic acid:— The scattering between the two maxima is so great that the position of the outer maximum can hardly be ascertained except by the comparatively sharp outer limit of it; the inner maximum, however, can be found with more certainty. There is also an area of small scattering around the direct spot as in the formic acid halo.

Propionic acid:— In this case the intensity of the outer maximum is much stronger than that of the inner one contrary to the case of acetic acid. There is no area of small scattering like that mentioned above, notwithstanding that the blackening of other parts is the same in degree.

Normal and iso-butyric acid:— The two maxima of the normal butyric acid halo were very diffuse and faint, and moreover the blackening of the other parts was abnormally great. It was almost impossible to describe the appearance of the figure. After the experiment was over, we learned from the maker, that this sample was very impure. The iso-butyric acid halo has a strong outer maximum and a diffuse inner one. There is a considerable outside scattering which has a fine limit at its outer end. The inside scattering is great, characteristic of the iso-compounds.

Iso-valeric acid:— The intensity of this halo has also a strong outer maximum and a faint inner one. Although there is adequate scattering in the other areas, this halo seems to be feebler than the iso-butyric acid halo.

Normal caproic acid:— There is a very intense maximum accompanied by a feeble scattering on both sides. The inner maximum is not very clear on account of its small size and a considerable scattering on the inside space which extends to near the direct spot.

Lactic acid:— In this halo the two maxima of intensity can scarcely be found by careful observation, because the blackening of the other areas is unusually intense and uniform. It has not been ascertained whether the cause may be attributed to the impurity of the sample, or the effect of the side chain OH in the molecule. However, it seems to be natural to attribute it to the former cause from the consideration of the case of normal butyric acid.

Oleic acid:— The halo shows two distinct maxima of nearly equal intensity with a comparatively slight scattering around them. The size of the inner maximum is not so small as might be expected from the consideration of the large number of carbon atoms in its

molecule. This may be another case indicating disagreement of the constitutional formula and the real form of the molecule.

4. Other Chain Compounds

Aceton :— There are two diffuse maxima of nearly equal intensity. The blackening of the other areas is marked especially on the inside of the maximum which extends to the direct spot.

Acetaldehyde :— This halo has also two maxima, the inner one being sharper and more intense than the outer. There is more scattering between the two maxima than in the other areas, especially the scattering around the direct spot is rather small as in the methyl alcohol, formic and acetic acid haloes.

Paraldehyde :— The outer maximum is so faint that its existence can only be found by careful observation, because the scattering between the two maxima is very great. The outside boundary of it is, however, very clear owing to the rather little large angle scattering. There is also a space around the central spot where the scattering is abnormally small as in the case of formic and acetic acid. The inner maximum is quite fine, and has a sharp limit towards the inside and a gradual decrease towards the outside. The general appearance of the figure seems to be between the diffuse halo of the cyclic compounds and the halo of the chain compounds, as might be expected from the chemical constitutional formula.

Ethyl-Ether :— The two maxima can be observed though they are not very clear. The scattering in the other areas is very faint. It was reported in the previous paper that the di-phenyl ether halo has only one comparatively sharp maximum of intensity. The difference can not easily be accounted for by the constitutional formula.

General Description of the Results

It has been already noted in the previous section that all paraffin haloes show only one maximum and the haloes of the other chain compounds examined in the present experiment two maxima. From the observation of the appearance and the dimensions of the figures, the outer maximum of the latter halo seems to correspond to that of paraffin haloes. If the real shape of these chain compounds may be allowed to belong to the cylindrical form, it is natural to consider that the spacings computed by Bragg's formula corresponding to this

maximum indicate the diameter of the cross-section of the molecule, and those corresponding to the inner maximum will indicate the length of the molecules. The constancy of the former spacings and the gradual increase of the latter with the increasing of number of carbon atoms in the molecules will easily be recognized. These values are given in the fifth column of Table I, where d_1 and d_2 are the diameters and the lengths respectively. If we assume that the molecules are so arranged that their lengths are parallel with each other and the centers of the cross-sections occupy the corners of a square, the lengths d_2 will be computed by the following equation,

$$d_2 = \frac{(\text{Molecular weight}) \times (\text{Mass of Hydrogen atom})}{d_1^2 \rho} \dots (1)$$

and, on the other hand, if the centers of the cross sections are assumed to occupy the corners of a hexagon and its center, which will be the closest packing, the lengths are computed to be

$$d_2 = \frac{(\text{Molecular weight}) \times (\text{Mass of hydrogen atom})}{d_1^2 \rho \sin 60^\circ} \dots (2)$$

The observed values of d_1 have generally more accuracy than those of d_2 owing to the greater size and sharpness of the outer maximum of intensity. The calculated values of d_2 from the above equations have been denoted by d_2' and d_2'' respectively in the last column of the same table. The lengths for the paraffin molecules are also calculated and given in the same column. As the observed values of d_2 are, in general, more or less greater than the calculated ones, a molecular volume of the observed dimensions is greater than the calculated ones. Therefore, the molecules must have closer packing, which would indicate that the molecules must interpenetrate somewhere. To settle this point, more investigation is needed.

The mean value of the spacing d_1 or the diameter of the cross-section is 5.01, 4.57 and 4.41 A.U. for the normal paraffin, alcohol and acid. Formic acid is excluded on account of its extraordinary small values. There is a tendency for the value to decrease on account of oxidation. For the iso-compounds of alcohols and acids, 5.08 and 5.07 A.U. are the mean values of d_1 which are larger than those of the normal compounds by 0.51 and 0.66 A.U. respectively. Moreover, all iso-compound haloes have more intense scattering in the space inside the maximum intensity than that of the corresponding normal compounds as noted in the previous section. This might be expected from

the constitutional formulae. The values of the spacing d_1 for the compounds having a double bond, such as amylene, allyl alcohol and oleic acid do not show any remarkable difference from those for the normal compounds, but the maxima are, in general, not so clear and intense. This may also be explained by the constitutional formulae. The molecules of the unsaturated compounds must be less symmetrical on account of the lack of two hydrogen atoms.

Next it is natural to expect that the value of d_1 for lactic acid, which has a side branch OH, should be somewhat larger than that of the corresponding chain compound. On the other hand the smallness of those for ethylene glycol and glycerine is quite unnatural and not to be expected from the consideration of the constitutional formula. Thus, the appearance of the haloes coincides in some cases with the presumption derived from the knowledge of the constitutional formula and not in other cases.

The observed values of the spacing d_2 for normal alcohols and acids increase gradually with the increase in the carbon atoms in the molecules. Though the values of the increase per carbon atom differ, the mean values are 0.61 and 0.84 A.U. for alcohols and acids respectively, which conform to some extent with the difference between the value of the spacing d_1 for the iso and normal alcohols and that for acids. Again, the values of the spacing d_2 for normal butyric acid, normal propyl and butyl alcohol are greater than those of the corresponding iso-compounds by 0.50, 0.69 and 0.59 respectively, which coincide with the expected values.

The size of the inner maximum of the haloes will become smaller and smaller owing to the increasing of the spacing d_2 . When the carbon contents become very large, d_2 will increase and the size of the inner maximum becomes very small, moreover the scattering on the inside part of it increases. Thus the observation of the exact position of it is very difficult as in the case of caproic acid, hexyl and heptyl alcohol, and especially in the geraniol halo, it can not be observed. The oleic acid halo is the exceptional case where two clear maxima are observed in spite of the large carbon content.

Each spacing d_1 of normal alcohol is slightly greater than that of normal acids, when the molecules containing the same number of carbon atoms, are made the basis of comparison for the other point there seems, within the scope of our experiment, to exist no gradual change in the appearances of the figures with the chemical constitutions.

Lastly it is interesting to compare the haloes of normal hexane and cyclohexane. The general appearance does not show any difference though the former halo has more scattering on both sides of the maximum intensity than the latter, but the former is much larger than the latter. The cyclohexane halo was noted in our previous paper, Part I.

In conclusion the writers wish to express their best thanks to Prof. S. Komatsu and Mr. R. Nakai who have kindly supplied many samples required for these investigations.

Plate I

Fig. 1. Formic acid.

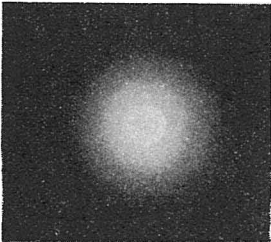


Fig. 4. n-Butyric acid.

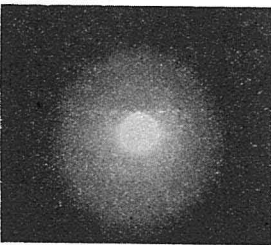


Fig. 7. n-Caproic acid.

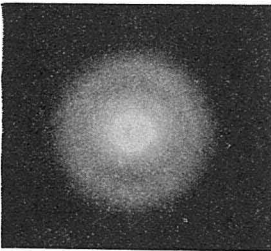


Fig. 10. Methyl alcohol.



Fig. 13. Iso-propyl alcohol.

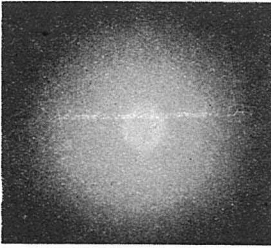


Fig. 2. Acetic acid.

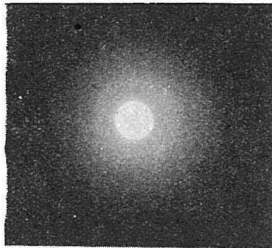


Fig. 5. Iso-butyric acid.

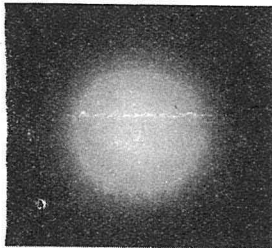


Fig. 8. Lactic acid.



Fig. 11. Ethyl alcohol.

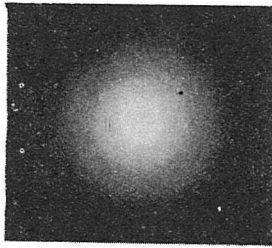


Fig. 14. n-Butyl alcohol.

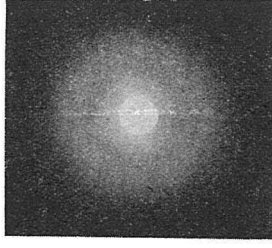


Fig. 3. Propionic acid.

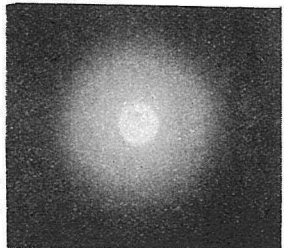


Fig. 6. Iso-valeric acid.

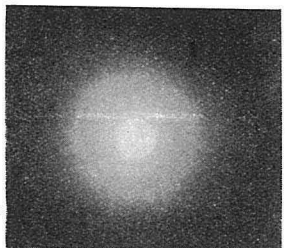


Fig. 9. Oleic acid.

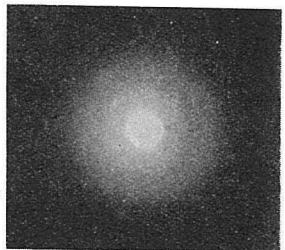


Fig. 12. n-Propyl alcohol.

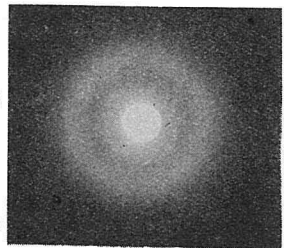


Fig. 15. Iso-butyl alcohol.

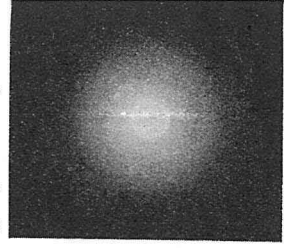


Plate II

Fig. 28. n-Pentane.

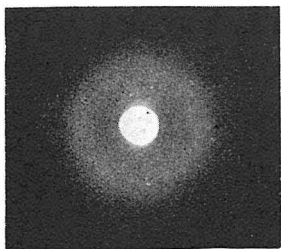


Fig. 29. n-Hexane.

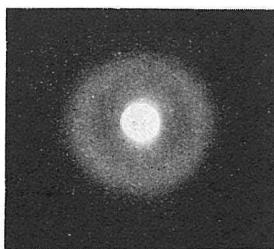


Fig. 30. n-Heptane.

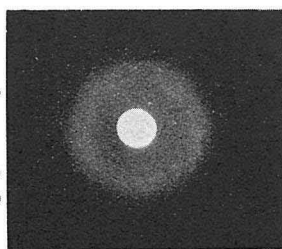


Fig. 25. Paraldehyde.

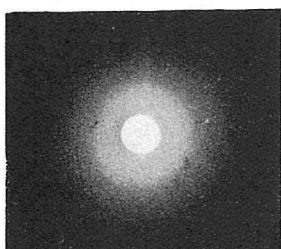


Fig. 26. Ethyl-ether.

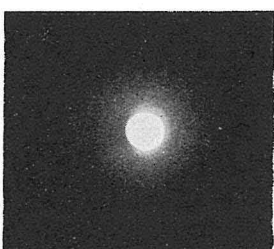


Fig. 27. Amylenc.

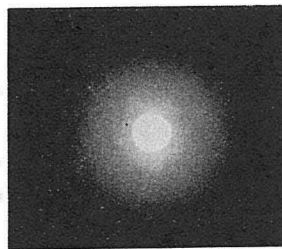


Fig. 22. Glycerine.

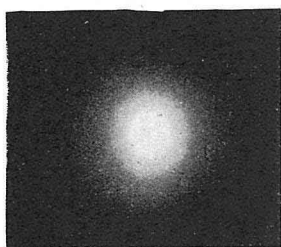


Fig. 23. Acetone.

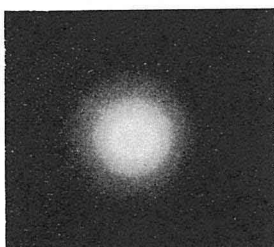


Fig. 24. Acetaldehyde.

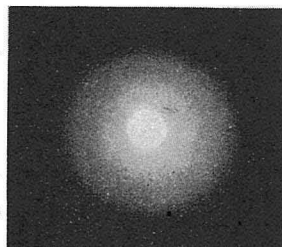


Fig. 19. Allyl alcohol.

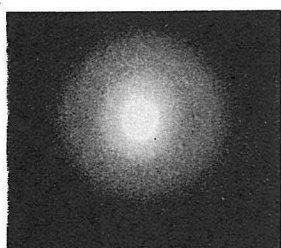


Fig. 20. Geraniol.

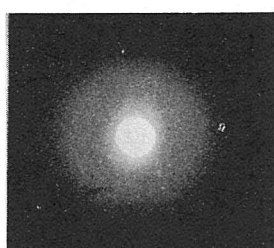


Fig. 21. Ethylene glycol.

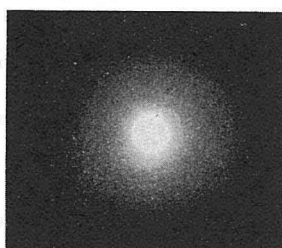


Fig. 16. Iso-amyl alcohol.

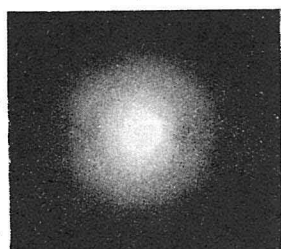


Fig. 17. n-Hexyl alcohol.

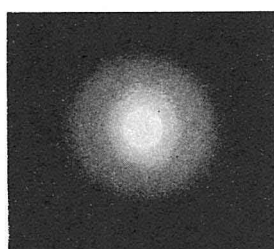


Fig. 18. n-Heptyl alcohol.

