Molecular Arrangement in Thin Films of Some Paraffins

By Kenzo Tanaka

Abstract

The arrangement in thin films of molecules of some pure paraffins and paraffin waxes formed on a polished copper plate was examined by the electron diffraction method. By observation of the change of the diffraction pattern with change of temperature, the transition-temperature of the film was measured (i. e. the temperature at which the arrangement of molecules at the surface of the film changes from a regular to an irregular one.) It was found that for pure paraffins the transition-temperature $t°C$ is in linear relation with the number of carbon atoms m in the molecule and is expressed as $t=m+58$. Similar relation was also found for paraffin waxes. The effect of mixing molecules of different chain lengths was observed with paraffin waxes and an empirical expression showing the effect is obtained. The change of the diffraction pattern with temperature is also discussed.

It is well known[1] that in thin films of some long chain organic substances formed on a flat surface of some solids the molecules are closely packed together side by side with their long axes at a steep angle to the surface of the solid. When these films are heated in vacuum the parallel arrangement of molecules at the surface of the film does not change appreciably even at a temperature somewhat higher than the melting point of the substance, but with further rise of temperature it is gradually destroyed by the heat motion of the molecules and at a certain temperature it becomes haphazard. This course can be followed in the reverse direction by lowering the temperature of the film, and the transition from irregular to regular arrangement of molecules takes place nearly at the same temperature as that of the transition from regular to irregular when the temperature is raised. This temperature has been called the "transition-temperature" of the film[2] and is nearly constant for a given substance.

Experiment

The following are the results of further examination of some pure

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1. For instance, C. A. Murison: Phil. Mag., **17**, 201 (1934).
2. K. Tanaka: These Memoirs, **21**, 85 (1938).
   " **22**, 377 (1939).

paraffins (C_mH_{2m+2}) and paraffin waxes by the electron diffraction method. The experimental procedure was the same as before and a small piece of copper plate polished with 0000 emery paper was used as the backing of the film in every case. Films of paraffins and paraffin waxes of different thickness were formed by dropping a drop of benzene solutions of different concentrations of the substance on the surface of the backing and by subsequent evaporation of benzene. Average thickness of the film was estimated from the volume of one drop of the solution and its concentration and the area of the film.

In measuring the transition-temperature by the electron diffraction method, care was taken to avoid the effect of prolonged bombardment of electrons on the same portion of the film since that causes the lowering to some extent of the observed transition-temperature. This was done by changing continuously the portion of the film under examination while it is bombarded or by making the electron bombardment intermittently on the same portion of the film.

Transition-temperature

Measurement of the transition-temperature was carried out with four different films of each substance having the average thickness of 8000 Å. The results are shown in Table I which shows that the transition-temperature is nearly constant for different films of equal thickness of each substance. Among them liquid paraffin did not show any regular arrangement of the molecules in the film treated by the same procedure as others. Parallel arrangement of the molecules in this film was obtained after it was once heated in vacuum at about

Table I

Substance	MeltingPoint °C	Transition-temperature °C			
$C_{17}H_{36}$	22°—22°.5	74°,	74°,	75°,	75°,
$C_{32}H_{63}$	70°—71°	88°,	88°,	88°,	88°
$C_{35}H_{72}$	73°—74°	91°.5,	91°.5,	92°	92°
$C_{64}E_{130}$	102°—102°.5	119°.5,	119°.5,	120°,	120°
Liquid paraffin		60°,	60°.5		
Paraffin wax	36°	70°,	70°,	70°.5,	70°.5
,,	42°—44°	73°.5,	73°.5,	73°.5,	74°
,,	52°—53°	79°,	79°,	80°,	80°
,,	60°—62°	89°,	90°,	89°,	89°
,,	68°—72°	97°,	97°.5,	97°,	97°

100°C for a while and then cooled below its transition-temperature. Such property was previously observed[1] with some unsaturated fatty acids and some oils.

Table II

Average thickness	Transition-temperature °C
0.1 mm	72°.5, 72°.5, 73°, 73°.5
8000 Å	73°.5, 73°.5, 73°.5, 74°
800 ,,	74°, 74°, 75°, 75°
80 ,,	73°.5, 73°.5, 74°, 74°
40 ,,	73°.5, 73°.5, 74°, 74°

Table II gives the results of measurement with a paraffin wax having the melting range of 42°–44°C. The thickness of the film was changed over a fairly wide range. Since the transition-temperature measured in this case is not markedly different for varying thickness of the film, it may be thought that this temperature is characteristic of the surface layer of the film with the thickness of one or a few molecules, and is one of the important properties characteristic of every one of these substances just as is its melting point.

In these hydrocarbon molecules it has been shown[2] that the carbon atoms are arranged in a flat zigzag chain and the distance between alternate carbon atoms is 2.54 Å. The length of the molecule is proportional to the number of carbon atoms in the molecule and the increase in length for the addition of one CH_2 group is 1.27Å.

The melting point of the substance belonging to this homologous series increases in a regular fashion with the number of carbon atoms in the molecule as is shown by Curve 1 in Fig. 1. By plotting the transition-temperatures of these
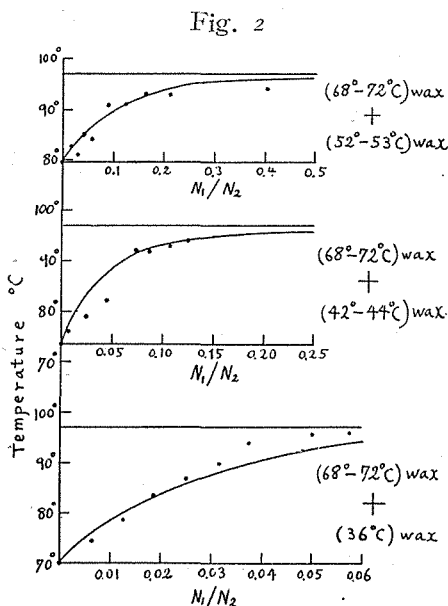
Fig. 1
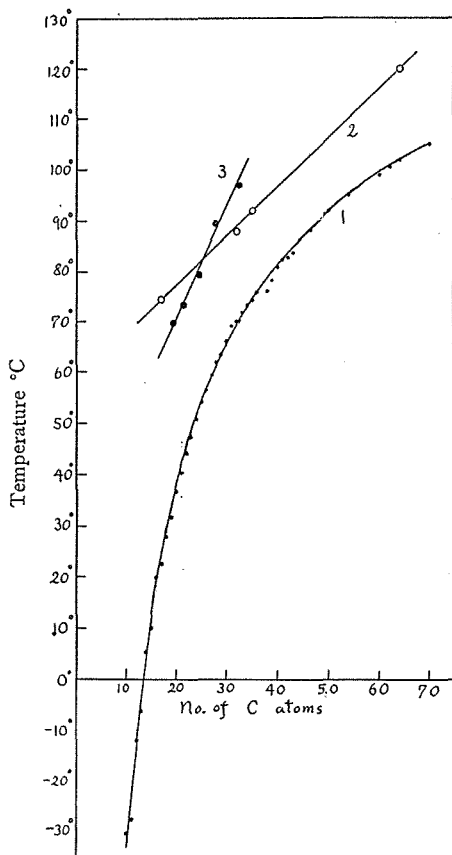
1. K. Tanaka: loc. cit.
1. A. Müller: Proc. Roy. Soc. A, **120**, 437 (1928).

substances shown in Table I in reference to the number of carbon atoms in the molecule, Curves 2 and 3 in Fig. 1 are obtained. Curve 2 is for pure paraffins and Curve 3 is for paraffin waxes. Since paraffin waxes are thoght to be mixtures of molecules having somewhat different lengths the average numbers of carbon atoms in the molecules were estimated from their average melting points. The fact that these two curves are nearly straight lines indicates that the transition-temperature of these substances increases linearly with the number of carbon atoms in the molecule. This fact may be simply explained as follows: As the temperature of the film rises, the mean amplitude of vibration of the molecules increases until kinetic energy of vibration overcomes the attractive force between molecules. At that temperature the transition takes place. Since the attraction acting most effectively between molecules of this kind is a lateral one which may be thought to increase proportionally with the length of the molecule or the number of carbon atoms in it, the transition-temperature should increase linearly with the number of carbon atoms in the molecule.

Curve 2 may be expressed simply as

$$t = m + 58$$

where t is the transition-temperature in °C and m is the number of carbon atoms in the molecule. Addition of one CH_2 group to the molecule causes an increase of 1° in t. Curve 3 has a different inclination with the coordinate axis from that of Curve 2 and this fact seems to be due to the effect of mixing molecules of different chain lengths. The effect of mixing molecules of different lengths upon the transition-temperature can, of course, be observed by mixing pure hydrocarbons of molecules of known lengths in any desired proportions. In the present case this examination could not be performed for lack of pure subs-

Fig. 2

tances. However, the general tendency of the effect may be observed by mixing paraffin waxes of different melting points. For this purpose three different kinds of mixtures of paraffin waxes having different melting points were prepared. These are $(68°-72°C)$ wax $+ (52°-53°C)$ wax, $(68°-72°C)$ wax $+ (42°-44°C)$ wax and $(68°-72°C)$ wax $+ (36°C)$ wax. Transition-temperatures of these mixtures are shown by dots in Fig. 2, where N_1/N_2 in abscissa is the ratio of the numbers of molecules of two kinds of waxes in the mixture. N_1 being for the wax having higher melting point and N_2 for a lower one. The transition-temperature of the mixture approaches very rapidly to that of the higher member with the increase of the number of longer molecules in the mixture. The effect is more marked for larger difference in the lengths of molecules of two waxes mixed, or for larger difference $m_1 - m_2$ in average numbers of carbon atoms in the molecules. The transition-temperature of the mixture may well be expressed in a form

$$t' - t_2 = (t_1 - t_2)(1 - e^{-u})$$

where $u = 0.016 \, (m_1 - m_2)^3 \, N_1/N_2$ and t_1, t_2 and t' are the transition-temperatures in °C of the two waxes mixed and of the mixture respectively. Curves in Fig. 2 show these empirical relations.

Diffraction Patterns

The diffraction pattern obtained by the reflection of electron beams at the surface of the film does not vary appreciably with the thickness of the film. But when the thickness of the film is reduced to the order of once or twice the molecular length, the whole pattern decreases in intensity and the pattern due to the backing of the film also appears. The diffraction pattern varies also with the temperature of the film. An example of the variation with temperature of the pattern of $C_{32}H_{66}$ is shown by the photographs reproduced in Plate I. Sharp straight layer lines with spots on them as obtained with paraffin molecules at room temperature become diffused and curved and the spots disappear at high temperatures just below the transition-temperature. at which even the diffused and curved lines also disappear. The disappearance of the spots shows the vanishing of a regular packing of the molecules at the surface of the film. The diffused and curved lines seem to be due to the fact that the molecules at the surface of the film are oscillating and are scattered in their orientation independently of each other with small angles about the

direction normal to the surface of the film. At and above the transition-temperature, the mean amplitude of vibration of the molecules becomes so large that the molecules can not arrange themselves in any regular manner, and the diffused curved lines in the
diffraction pattern disappear. The manner of variation of the diffraction pattern with temperature is similar in pure paraffins and paraffin waxes. The photograph (f) in Plate I is obtained with a film
which was heated above the transition-temperature and then cooled
rapidly to the room temperature. The layer lines became diffuse and
curved to some extent when compared with those before heating.
This seems to be due to somewhat scattered orientation of many small
crystals of paraffin, which is caused by a rapid cooling in vacuum
from the temperature higher than the transition one to the room
temperature. This effect is more pronounced in the case of pure
paraffins which are more easily crystallizable than paraffin waxes.

The mean amplitude of oscillation of molecules about a fixed
direction at any temperature can be estimated as follows: For simplicity we assume a model of paraffin molecule consisting of m carbon
atoms arranged in a straight line with a constant spacing d. The
intensity of the electron wave scattered in any direction by such a
model is proportional to

$$\psi^2 \frac{\sin^2 \frac{m\delta}{2}}{\sin^2 \frac{\delta}{2}}$$

where ψ is the amplitude of the electron wave scattered by a carbon
atom and δ is the phase difference between the scattered beams by
two successive atoms. The amplitude ψ due to a carbon atom is
expressed as

$$\psi = \frac{1}{r} \frac{e^2 m}{2h^2} (Z-f) \frac{\lambda^2}{\sin^2 \frac{\theta}{2}}$$

where Z and f are the atomic number and the scattering factor of the
carbon atom respectively, λ the wave length of the electron beam, θ
is the scattering angle and others have the usual meanings. The
intensity maxima of the scattered radiation appear when $\delta/2$ is an
integral multiple of π, at which the value of $\sin^2 \frac{m\delta}{2} / \sin^2 \frac{\delta}{2}$ becomes
m^2. The intensity distribution along the second order layer line calculated in the case of $d = 2.54$ Å, $\lambda = 0.05$ Å and D (the distance bet-

ween the specimen and the photographic plate)=500 mm, when the incident electron beam proceeds normally to the axis of a molecule standing perpendicular to the surface of the film, is shown in Fig. 3 where x is the distance along the layer line measured from the plane of incidence. The intensity falls fairly rapidly with increasing scattering angle.

In Fig. 4, using polar coordinate, let the electron beam proceed along the direction OO' $\left(\frac{\pi}{2}, 0\right)$ upon a molecule whose axis is OP (θ_1, ϕ_1) and let ON be the direction normal to the surface of the film. Next let the diffracted beam OD have a scattering angle θ and make an angle ϕ with the plane of incidence. The diffraction maxima appear when

$$\frac{n\lambda}{d} = \cos\theta_1 \sin\theta \cos\phi + \sin\theta_1 \cos\phi_1 (\cos\theta - 1)$$
$$+ \sin\theta_1 \sin\phi_1 \sin\theta \sin\phi.$$

If we represent $\overline{OO'}$ by D and the coordinates of any point on the photographic plate by r, ϕ, the above condition becomes
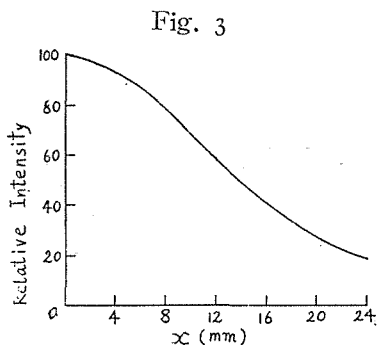
$$\frac{n\lambda}{d} = \cos\theta_1 \cos\phi \frac{r}{\sqrt{D^2+r^2}} + \sin\theta_1 \cos\phi_1 \left(\frac{D}{\sqrt{D^2+r^2}} - 1\right)$$
$$+ \sin\theta_1 \sin\phi_1 \sin\phi \frac{r}{\sqrt{D^2+r^2}}.$$

As r is very small compared with D in the present case, we may write the above condition as

$$\frac{n\lambda D}{d} = \cos\theta_1 \, r \cos\phi + \sin\theta_1 \sin\phi_1 \, r \sin\phi$$
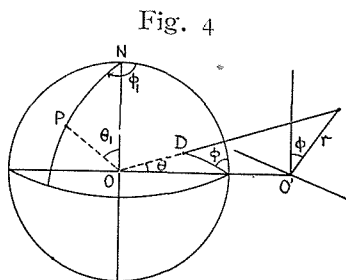
For given values of n and θ_1 this is an equation of a family of straight lines of parameter ϕ_1 which pass through a common point $(n\lambda D \sec\theta_1/d, 0)$. When all the molecules in the film are at a constant inclination θ_1 and distributed uniformly about the direction normal to the surface of the film, the layer lines are obtained from the above equation by giving various values to ϕ_1 ranging from 0 to 2π. As the incli-

Fig. 3

Fig. 4

nation θ_1 of the molecule increases the common point recedes far from
the direct spot, along the line $\phi = 0$ and the angle of divergence of
the bundle of layer lines which is equal to $2\theta_1$ becomes larger.

The most intense point on each layer line has the minimum value
of θ and is at the foot of the perpendicular drawn on the line from
the direct spot. The intensity falls rapidly along the line as the dis-
tance from this point increases. For the most intense point on the
line obtained with given values of θ_1 and ϕ_1, we get

$$r = R \sec \theta_1 \cos \phi$$

and $\qquad \tan \phi = \tan \theta_1 \sin \phi_1,$

where $R = n\lambda D/d$. By changing the value of ϕ_1 for a given value
of θ_1 these equations represent a circle having a diameter of $R \sec \theta_1$

Fig. 5
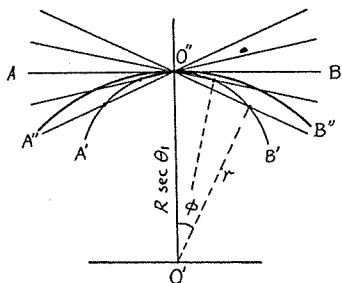
as shown by the curve A'O''B' in Fig.
5. If we assume that the molecules
having a constant value of θ_1 are distri-
buted uniformly with respect to ϕ_1, as
will naturally be the case, then the
layer lines due to them will be a system
of an infinite number of straight lines
intersecting at the point O'' as is shown
in Fig. 5. If the intensity is the same
on every point on the lines, the locus
of the centre of gravity of the layer lines would be the straight line
AO''B. But the intensity at a point on a layer line decreases rapidly
as we recede from the foot of the perpendicular drawn from the point
O' to the layer line ; and consequently the locus of the centre of
gravity of the layer lines will occupy a position between the straight
line AO''B and the circle A'O''B', as is represented by the curve
A''O''B'' in Fig. 5. This mode of rough and rather qualitative ex-
planation of the appearance of diffuse and curved layer lines is almost
the same as that given by Murison.[1]

But the actual case will be more complicated. When the tem-
perature is raised to somewhat below the transition-temperature, the
inclination θ_1 of the axes of the chain molecules of paraffin will also
be scattered to some extent around the ideal orientation $\theta_1 = 0$. The
locus of the centre of the layer lines as stated above will now become
diffused, keeping the general aspect of the curve as A''O''B'' unaltered

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1. C. A. Murison: loc. cit.

as is actually observed and reproduced in Plate I. In the following the effect of the scattering of molecular orientation will be considered more minutely from the view point of the oscillation of the molecular axes by thermal agitation.

Since any one point on the line $\phi = 0$ corresponds to a certain value of θ_1 only, and the intensity of all the layer lines which correspond to various values of ϕ_1 and pass through this point is equal at this point, the intensity at any point on the line $\phi = 0$ is proportional to the number of molecules at the inclination θ_1 corresponding to that point. If for instance all the molecules at the surface of the film are in oscillation with a definite angular amplitude Θ, the intensity at a point on the line $\phi = 0$ which corresponds to a certain value of θ_1, is inversely proportional to the angular velocity ω of oscillation of the molecule in passing through this inclination θ_1. The intensity is therefore proportional to

$$\frac{\psi^2}{\omega} = \frac{c\psi^2}{(\cos\theta_1 - \cos\Theta)^{\frac{1}{2}}}$$

And the intenity distribution is therefore expressed along the line $\phi = 0$ by

$$\frac{c\psi^2}{\left(\dfrac{R}{r} - \dfrac{R}{r_m}\right)^{\frac{1}{2}}}$$

where $r_m = R \sec\Theta$. This indicates that the intensity is maximum at $r = r_m$ corresponding to the point of the angular amplitude Θ.

The intensity at any one point (r, ϕ) on the photographic plate depends upon the number of layer lines passing through this point and the intensities of the layer lines at that point. Both extreme lines of the bundle of layer lines passing through the point (r, ϕ) coincide with the tangential lines drawn from the point to the circle of radius R having the centre at O'. If we denote the intercepts of these two tangential lines with the line $\phi = 0$ by r_1 and r_2 respectively, then

$$r_1, r_2 = r\cos\phi - r\sin\phi \frac{r^2\sin\phi\cos\phi \pm R\sqrt{r^2 - R}}{r^2\sin^2\phi - R^2}.$$

The intensity at the point (r, ϕ) is then proportional to

$$c\psi^2 \int_{r_2}^{r_1} \frac{d\rho}{\left(\dfrac{R}{\rho} - \dfrac{R}{r_m}\right)^{\frac{1}{2}}} = \frac{c\sqrt{r_m}}{\sqrt{R}}\left[r_m\sin^{-1}\sqrt{\frac{r}{r_m}} - \sqrt{r}\sqrt{r_m - r} \right]_{r_1}^{r_2}$$

where ρ is the intercept on the line $\phi = 0$ of a layer line passing through the point under consideration. The range in which any layer line of the order n exist is given by

$$\frac{r \cos \phi - r_m}{r \sin \phi} \leqslant \tan \Theta \quad \text{and} \quad r \geqslant R$$

and

$$\frac{r_m - r \cos \phi}{r \sin \phi} \leqslant \tan \Theta \quad \text{when} \quad \phi > \Theta$$

An example of the intensity distribution along the line $\phi = 20°$ due to the layer lines of the second order when $\Theta = 30°$ calculated by the equations is shown in Fig. 6.

Fig. 6
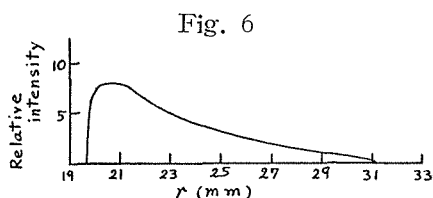
If we assume that all of the molecules at the surface of the film are oscillating independently of each other with a definite angular amplitude, the amplitude can be obtained by measuging the intensity distribution along any one line of constant ϕ. But the actual case will be more complicated and the amplitude of oscillation will be different for different molecules in the film. Actually the maximum inclination of the molecules about the normal direction of the film does not increase appreciably till the temperature approaches very near to the transition-temperature at which the curved layer lines fade out rapidly. Furthermore in the case of higher member paraffins the spot on the layer lines exists together with the lines up to the transition-temprature where both fade out simultaneously. This shows that a fairly large number of molecules are still arranged in crystal lattice probably due to their stronger lateral adhesion and do not oscillate freely till the transition-temperature is reached. In the following the maximum inclination of molecular oscillation due to thermal agitation was estimated roughly by comparing only the breadth of the curved layer lines in the actual diffraction pattern obtained at any temperature, with that occupied by a system of layer lines which correspond to various values of θ_1 ranging from zero to the maximum value Θ for which also various values taken at the interval of $5°$ were assigned. The results are shown in Fig. 7. where dots and small circles show the maximum inclinations of the molecules in degrees at those temperatures : representing by a dot the case where the diffraction spots coexist with the layer lines, and by a small circle the case where no spot appears on the layer lines. The relation between

the temperature t and the maximum inclination Θ of molecular oscil-
lation thus estimated was seen to be expressed approximately by

$$\Theta = \frac{2m}{T-t}$$

where T is the transition-temperature and m is the number of carbon
atoms in a paraffin molecule. The curves shown in Fig. 7, which
were drawn by the above formula agree approximately with actual
observation.

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and Mr. K. Fuchino for their kindness in furnishing pure specimens
of paraffin and to Prof. U. Yoshida for his invaluable suggestions
given to the writer in carrying out the present experiment.
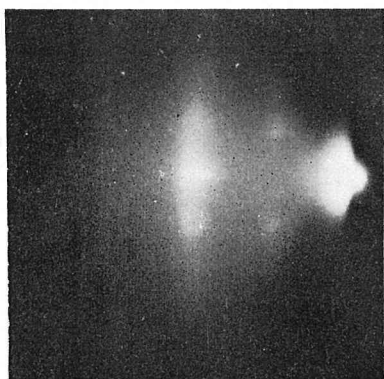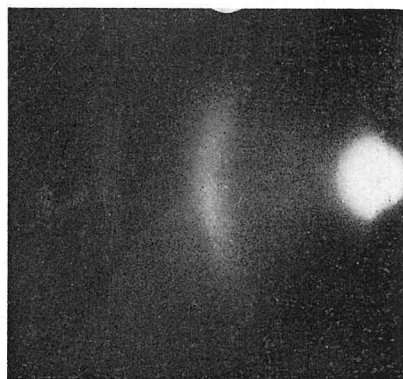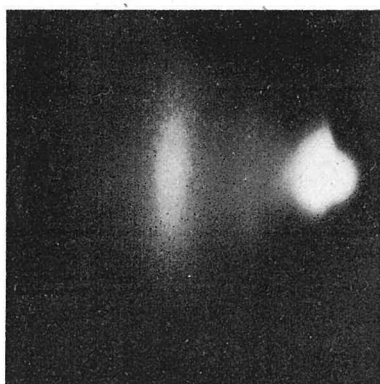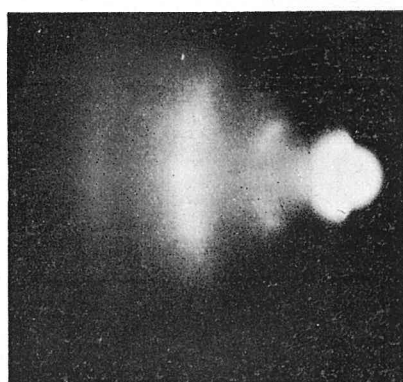
Fig. 7

Temperature °C
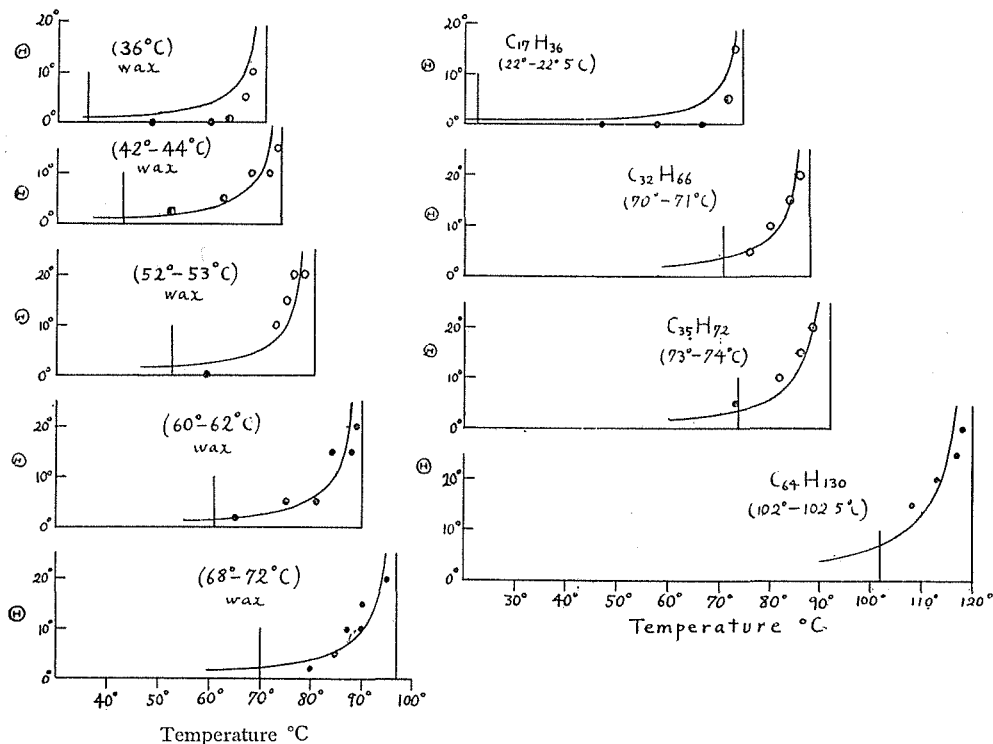
Plate I
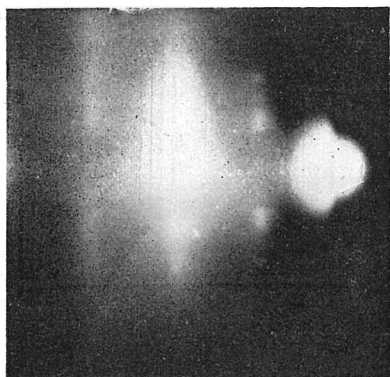
(a) 22.5°C
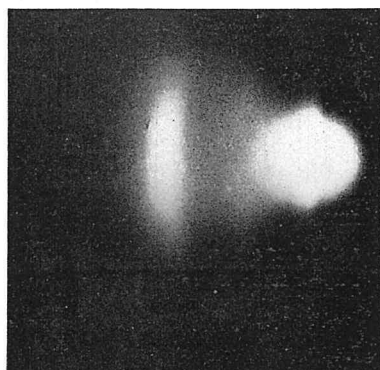
(d) 80°C

(b) 70.5°C

(e) 86°C

(c) 77°C

(f) 21.5°C