

Molecular Arrangement in Thin Films of Some Fatty Acids and Oils

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Abstract

The arrangement of molecules in thin films of some fatty acids and oils smeared on a polished copper plate was examined by the electron diffraction method. In some cases heating of the film in vacuum at a suitable temperature changed the manner of arrangement of the molecules in the film from irregular to regular. The manner of arrangement of the molecules in thin films of oils was found to depend upon the history of preservation of the oils. Classification of the property of oils was made in this respect. From the observation of the change of diffraction pattern with temperature the transition-temperature of the film (melting temperature of a thin surface layer having a regular molecular arrangement) was measured. It was in the ranges of 120°-130°C for stearic and palmitic acids, 55°-65°C for oleic and linolic acids and 50°-60°C for some oils.

Transition-Temperature

In a preceding paper¹ the change, with temperature, of the electron diffraction pattern caused by films of grease, vaseline and paraffins smeared on a polished copper plate was examined, and it was observed that at some elevated temperatures the parallel arrangement of the long-chain molecules of these substances is gradually destroyed and with further rise of temperature it becomes haphazard. This temperature at which the regular arrangement of molecules changes to an irregular one was called the transition-temperature of the film. This temperature is different for different substances, and for a given substance it depends somewhat upon the thickness of the film. Since the transition from regular to irregular arrangement of molecules is reversible and is considered to be caused by the heat motion of the molecules, the transition-temperature may be looked for as the melting point of a film having the thickness of one or a few molecules. So far as the present experiment is concerned it was generally higher than the ordinary melting point of the substance as a mass.

The substances previously examined by the writer gave rise to the

1. K. Tanaka: These Memoirs, 21, 85 (1938).

grease-pattern and no appreciable change of the pattern was observed by varying the thickness of the film. For thick films of these substances it may be considered that besides a thin layer having the regular arrangement of the molecules at the free surface of the film, another thin layer having the same regular molecular arrangement is formed at the film-metal interface. And thus when the films become very thin these two layers unite to a single layer having the same regular molecular arrangement. The transition-temperature for these two cases was nearly equal for the same substance, but in some cases it was somewhat lower for the thin film. For substances such as unsaturated fatty acids or oils the diffraction pattern showing the regular molecular arrangement is obtained only when the film is very thin. In such cases the regular orientation of molecules is caused only by the effect of the solid surface forming the backing of the film, whose effect becomes too weak to give rise to the regular molecular arrangement at the free surface of the film when its thickness is increased.

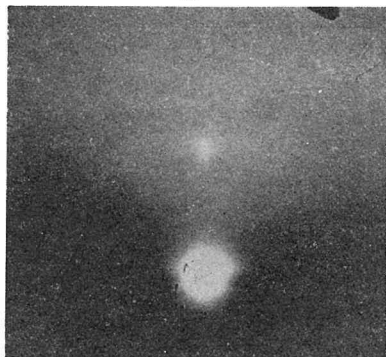
The following are the results of further examination of some fatty acids and oils. The experimental procedure was the same as before and a small piece of polished copper plate was used as the backing of the film in every case.

Fatty acids

Palmitic and stearic acids belonging to saturated fatty acid were examined. With thick films of these substances no diffraction pattern was obtained owing to the effect of the charge accumulated on the surface of the film. Thin films of both acids gave rise to a pattern consisting of the layer lines, rings and spots as obtained by other investigators. When these thin films are heated in the evacuated diffraction apparatus the pattern due to the regular molecular arrangement can be maintained up to a temperature which is much higher than the ordinary melting point of the substance. The transition-temperatures of the two acids thus measured were found to be in the same range of 120° – 130° C.

Observations were then carried out with two kinds of unsaturated fatty acid, oleic and linolic acids. Thick films prepared by putting a drop on the backing and by allowing it to drain off, gave only a diffuse halo. This shows that in the free surface layer of these films the molecular arrangement is haphazard. Diffraction patterns obtained with thin films prepared by rubbing the thick films with a filter-paper were

Fig. 1



Oleic acid

Fig. 2



Linolic acid

similar to those of thick films. But when these thin films were heated in the evacuated diffraction apparatus for a while at a temperature of about 100°C and then cooled to the room temperature, they gave the grease-pattern showing that the arrangement of molecules in the film becomes regular. The patterns thus obtained are shown in Figs. 1 and 2 respectively.

The effect of heating in causing the regular arrangement of the molecules may perhaps be due partly to the ejection of some gases and volatile impurities which are included in the substance and at the film-metal interface and interrupt the orientating effect of the backing to the free surface of the film, and partly to the favourable conditions for the molecules to rearrange themselves in a regular manner at an elevated temperature.

Transition-temperatures of these thin films were found to be in the range of 55° – 65°C for both acids.

Oils

Many kinds of oils: vegetable, animal and mineral, were also examined. When the film is thick every oil tested showed no sign of regular molecular arrangement even after heating it in the vacuum. When the film is thin, though most kinds of oils also did not show the regular molecular arrangement, there was a few which gave rise to the grease-pattern. This pattern becomes diffuse and finally a halo with increasing thickness of the film. Thus the regular arrangement of the molecules in this case is considered to be due to the effect of backing to cause it at the free surface of the film. It is convenient to classify the oils possessing the property stated above as Class I.

Among the oils other than those of Class I some gave the grease-pattern with their thin films when they were subjected to a similar heat treatment in vacuum as before (Class II), and the others did not show any regular arrangement of the molecules even with the heat treatment (Class III). In some cases similar heat treatment in air caused an effect upon the arrangement of the molecules which is less appreciable than in vacuum. The property of the oils belonging to Class II, that is, to give the grease-pattern by vacuum heating, could not be preserved for a long time by exposing the oil to air, and it changed to that of Class III. Such classification of oils into three classes is not related necessarily to different kinds of oils, and even the same kind of oil manifests two or three different properties characteristic to the three different classes according to its state of preservation. The time of exposure to air which is necessary to cause such transformation, is very different for different oils ranging from a few days to several months. When an oil having the properties peculiar to Class I or Class II is transformed by being exposed to air to Class III it shows no regular diffraction pattern even with a vacuum heating of much higher temperature.

A similar effect was observed in the case of unsaturated fatty acids. The diffraction pattern obtained after the vacuum heating became more diffused with increasing duration of the exposure of the acids to air. The patterns shown in Figs. 1 and 2 were obtained with the acids taken out freshly from sealed bottles. Thus a profound attention should be paid to the history of preservation of an oily substance in studying the manner of its molecular arrangement on a smooth surface of a solid.

When an oil having the property of Class II is boiled in an evacuated glass tube, it preserves for a long time its property of taking the regular molecular arrangement by the vacuum heating. Therefore the change of the property of oils to lose its property of taking the regular molecular arrangement when exposed to air seems to be caused primarily by its absorption of air.

The transition-temperatures of thin films of various oils belonging to Classes I and II were measured. They were in nearly the same temperature range from 50° to 60°C.

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