LOW ANGLE X-RAY MEASUREMENTS ON DENSELY PACKED COLLOIDAL SYSTEMS—WOOL

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ABSTRACT. Low angle x-ray methods have been applied to determine the size of the scattering inhomogeneities in wool assuming it to belong to the densely packed colloidal system after Guinier methods of evaluation. The absence of particle scattering in such systems is made clear.

INTRODUCTION

By using the low angle scattering camera of Kratky it has been possible to determine the size of the large sized particles. The difference between particle scattering as in the case of dilute colloidal systems and scattering by matter in densely packed colloidal systems as considered by Porod (1951) and Kratky (1952) becomes clear. It has been possible to determine the thickness of the layers assuming wool to be distributed in layers with free spaces in between.

EXPERIMENT

A sample of wool of the type Greany Lincoln Ewes from England was the substance investigated. In order to remove any amount of impurity and fats the sample was washed with soap, cleaned in a stream of distilled water, cooked with 1:3 mixture of aether and alcohol for 25 hours, in cyclohexane for 8 hours and finally in benzene for 8 hours to attain high degree of purity. Cooking the sample for longer periods produced no effect on the x-ray diagram, as by the above process most of the fats were removed and the substance arranged itself in layers with free spaces in between. It was then stretched to avoid any curling, its density determined and an amount with a definite cross-section was introduced into a Mark capillary, the scattering due to the empty capillary container having been determined previously. The sample had the following constants :-

Length	35 mm.
Weight	31 mg.
Density	0.32gm/c.c.
Thickness	1.88 mm. (This was also the internal diameter of the Mark capillary.)

Exposures were taken with the empty capillaries, exposure time in each case being 2/3 of that for the corresponding sample. This is due to the difference in absorption between the container glass and the sample, the latter being a strong absorber exposure times were less therefore for empty containers. The capillary containing the sample was so placed that the length of the primary beam was parallel to the fibre axis. Therefore the diffraction pattern should correspond to the equator representation of the fibre diagram of "O" Kratky (1955) or Polanyi (1921).

The apparatus used is the well known small angle scattering camera of Kratky (1958) fitted with a photographic arrangement. As it is desired to photograph the scattered intensity from very small angles up to high angular values, in the small angle region, it is not possible to obtain the complete picture in a single photograph. When the time of exposure is large, the scattered intensity as registered by the photographic film at very small angles is so strong that it cannot be measured by densitometer. For too short exposures, intensity corresponding to larger angles being very weak, cannot be registered by a photographic film at all. Therefore it was decided to photograph the whole region in parts by keeping the primary beam shutter of the apparatus at various heights following the procedure of Kratky outlined in this paper. A series of photographs were obtained with different times of exposure by adjusting the primary beam shutter at different heights. The highest of the primary beam shutter and the corresponding exposure timings are given below.

Height of the primary beam shutter in 1/100 mm.	Exposure time in minutes
185	12
195	24
207	48
221	96
238	192
260	384

The time of exposure varied from 12 mins. to 384 mins., thus photographing a range corresponding to Bragg values of 800 Å to 50 Å for $\lambda = 1.54$ Å in stages. After this the corresponding densitometer curves were obtained under identical conditions. Each partial curve represents a particular angular range of diffraction. They are plotted in parts in Fig. I. After this the total curve can be obtained by multiplying the partial curve intensities with their respective time factors. The experimental measurements and their relative transformations are given in Table I. A Siemens apparatus fitted with a copper target was

employed in the present investigation. The balanced filter method due to Kratky (1943) was utilized to obtain the above partial intensity curves due to CuKα radiation. The entrance slit of the low angle camera was 0.11 mm. and the film sample distance was 135 mm.

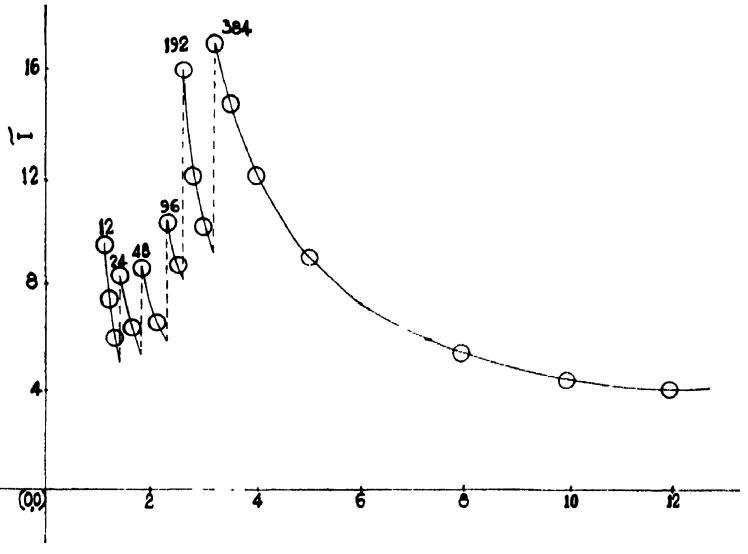

Fig. 1. ap = 13.5×25.4

DISCUSSION AND THEORY

As wool is an oriented substance one can proceed with the smeared-out curve and no slit correction is necessary. Moreover due to a very large difference in the scattered intensity of the innermost and the outermost portions of the curve, it is only convenient to plot log $\tilde{I}$ versus m to know the exact nature of the scattering curve (Fig. 2). Here $\tilde{I}$ is the smeared-out intensity and m is the

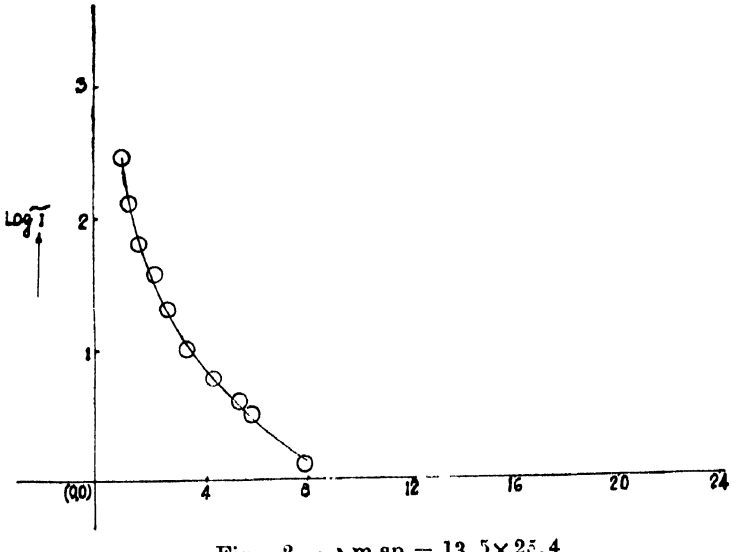

Fig. 2. ⟶ m ap = 13.5×25.4

distance from the centre of the primary beam measured along the densitometer curve and is therefore a function of the scattering angle 2θ. The double logarithmic plot log $\widetilde{I}$ versus log m is a straight line of slope -2.86 (Fig. 3).

According to Porod (1953) the tail portion of the smeared-out scattering curve of a general two phase system decreases like k/m^3 where k is a measure of the interface of the two phases. As usual m is given by

$$2\theta = m/ap$$

where 2θ is the angle of scattering, "a", the film sample distance and "p" is the transformation factor. The intensity I can therefore be expressed as

$$\widetilde{I} = K/m^3$$

$$\therefore \quad \log \widetilde{I} = \log (k/m^3)$$

$$\therefore \quad \log \widetilde{I} = \log k - 3 \log m$$

$$\therefore \quad \frac{d \log \widetilde{I}}{d \log m} \ldots 3, \text{ since } \log k \text{ is a constant.}$$

As tan α, the slope of the straight line in the double logarithmic plot is about - 3, (Fig. 3). this exactly represents the tail portion of such a smeared-out curve for accessible scattering angles. It is not possible therefore to determine the size of the scattering inhomogeneities as a whole. We can estimate that it must only be larger than the largest measurable Bragg-value of about

$$D = \frac{\lambda}{1} \; ap \text{ Å}$$

i.e. $D = 1.54 \times 13.5 \times 25.4 = 520$ Å; for $\lambda = 1.54$ Å, $a = 13.5$ and $P = 25.4$.

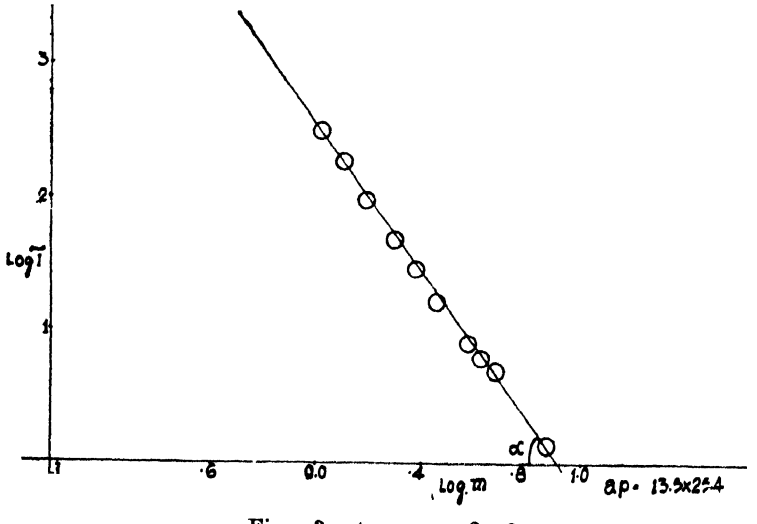

Fig. 3. tan $\alpha = -2.86$

Assuming micelles of variable thickness as model for the scattering system (Kratky and Porod, 1949), we can hope to obtain the mean thickness from the Guinier plot log $\widetilde{I}m^2$ versus m^2. From such a curve one can easily get, on drawing two asymptotic tangents at the two extremities, two values of the thickness factor of about 60 Å and 125 Å respectively.

TABLE I

Measurements on wool, filter difference method

1 m	2 I	3 F	I	$\times 4$ $\tilde{I} \cdot F$
1.1	9.3		293.6	
1 2	7 3	32	229.6	
1 3	5.8		181.6	
1.4	8.1		125.6	
1 6	6.1	16	93 6	
1 8	8 4		63.2	
2 1	6 35	8	46.8	
2 3	10 2		36 8	
2 5	8.5	4	30 0	
2 6	16 0		28 0	
2.8	12 0		20 0	
3 0	10 0	2	16 0	
3.2	13 0		13 0	
3.5	10.7		10.7	
4.0	8.0		8.0	
4.5	6.2	1	6.2	

I—Intensity not corrected for time factor.
F—Time factor.

$\tilde{I}$—Smeared-out intensity
$\times$—Corrected for the background intensity.

A thorough theoretical handling of the problem of low angle scattering is due to Porod (1949) which applies to fully oriented systems like regenerated cellulose. The scattering of such a system treated after Babinet's reciprocal relation, after certain assumptions, leads to a scattering function ϕ_2 resulting out of interparticular interference. This effect is very important where the distance between neighbouring particles is much smaller than the dimensions of the particles themselves. The function ϕ_2 increases rapidly to very high values as the

scattering angle 2θ approaches zero. When $2\theta = 0$ this intensity becomes infinite. That is why in the case of wool, irregular system not highly oriented, the scattering curve, (Fig. 2), is very steep and runs almost parallel to the Y axis for very small values of 2θ. In this case the particle scattering is practically absent due to the irregularity of the free space and the occupied space.While interparticular effects are predominant. The scattered intensity speaks about the spread or extension of the micelle system.

CONCLUSION

The size of the scattering inhomogeneities in wool are larger than 520 Å. Interparticular interference is predominent in the system.

REFERENCES

Kratky, O., 1942, *Naturwiss*, **30**, 542.
" (1955), *Physik der Hochpolymeren*, **3**, 288.
Kratky, O. and Scala, Z., 1958, *Z. Elektrochemie*, **62**(1), 66.
Kratky, O. and Porod, G., 1949, *J. Colloid Sci.*, **4**, 36.
Kratky, O. and Sekora, A., 1943, *Naturwissenschaften*,, **31**, 46.
Polanyi, M., 1921, *Z. Physik*, **7**, 149.
Porod, G., 1951, *Kolloid, Z*, **124**(2), 83.
Porod, G., 1953, *Kollid-Z.*, **133**, 16.
Porod, G., 1949, *Acta Physica Aust.*, **3**(1), 66.