DETERMINATION OF THE RELATIVE DISTRIBUTION OF LAYERS IN DENSELY PACKED COLLOIDAL SYSTEMS—WOOL

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ABSTRACT. This paper deals with the determination of the distribution of layers in wool assuming it to belong to the Hohl-raum system, substances packed in layers with free spaces in between. In a paper by one of us, (Ratho, 1964), Guinier methods (1937) have been applied to determine the thickness factor in wool. In the present paper we have assumed a particular thickness factor of 61 λ or 94 Å, for $\lambda = 1.54$ Å, as the mean thickness of layers which is also the probable mean thickness of different samples of wool belonging to the general micelle system. Porod (1949) in his paper on such systems has introduced a relative fluctuation factor δ given by

$\delta = \frac{\Delta}{d_0}$, where d_0 is the mean distance between layers, $\Delta = \{(d-d_0)^2\}^{1/2}$ is the root mean square fluctuation and d is the distance between any two layers. We have here tried to find out the relative distribution by calculating the theoretical scattering curves with different relative fluctuation factors $\delta = 0.2$, 0.4, 0.6, and 0.8, for the thickness factor of 61 λ and have tried to show the agreement between the theoretical and the experimental results. We have also drawn the theoretical curves with these four fluctuation factors for two other thicknesses of 40 λ and 80 λ which are also probable as they give rise to a mean thickness about 61λ. It is found that with the mean thickness of 61λ alone the theoretical and the experimental scattering curves, agree most in the high intensity region when $\delta = 0.4$ and in the region of low intensities when $\delta = 0.8$. From this one can conclude that the thicker layers in the sample occur more frequently than the thinner ones.

EXPERIMENT

The substance investigated is a sample of wool of the variety Scottish Blackface from England. The experimental arrangement and the procedures were the same as reported in the paper referred to above (Ratho, 1946). As wool is an oriented substance one can proceed with the smeared-out intensity, $\tilde{I}$, no slit correction being necessary. The experimental intensity $\tilde{I}$ is converted to a scattering function $\phi(s)_{Ex}$. as after Porod (1949) where we have taken $\tilde{I} = I_0 S\, \phi(s)_{Ex}$, where I_0 is the incident intensity and S is a scattering factor ; $\phi(s)_{Ex}$ represents the experimental value of the scattering function $\phi(s)$ and

$$s = \frac{4\pi \sin \theta}{\lambda} = \frac{4\pi\theta}{\lambda}, \text{ for } \theta \to 0.$$

The scattering angle θ is represented in terms of μ where

$$\mu = 244\pi\theta.$$

The $\phi(s)_{Ex}$ and μ values are shown in the Table I, the angular range studied being from

$$\theta = 0.27 \times 10^{-3} \text{ to } \theta = 3.93 \times 10^{-3} \text{ in radians.}$$

THEORY AND DISCUSSION

A large volume of theoretical and experimental works on densely packed colloidal systems have been published by Kratky (1938) and Porod (1949). The scattering of fibrous substances like regenerated cellulose and wool have been treated after Babinet's reciprocal relation in optics and they have come to the conclusion that scattering should not come under particle-scattering while interparticle-scattering plays a predominant role. Porod (1949) in his paper arrived at a scattering function $\phi(s)_{Th}$, theoretically which can be split up into two functions ϕ_1 and ϕ_2 where

$$\phi(s)_{Th} = \phi_1 + \frac{1}{n}\phi_2$$

Here ϕ_1 represents the particle-scattering while ϕ_2 represents the interparticle scattering.

Assuming the particle scattering to be completely absent one can represent the theoretical scattering function, after certain approximations,

$$\phi(s)_{Th} = \frac{1}{n}\phi_2 \text{ as}$$

$$\phi(s)_{Th} = \frac{(1 - \cos\mu \cosh \mu^2 \delta^2/2)}{(\cosh \mu^2\delta^2/2 - \cos\mu)^2}$$

where $\mu = sd_0$.

For small values of θ and for a mean thickness d_0 of 61λ it can be easily seen that

$$\mu = 244\pi\theta$$

From the experimental measurements one gets the scattering intensity $\tilde{I}$ which can be represented as

$$\tilde{I} = I_0 S \phi(s)_{Ex}$$

where I_0 is the incident intensity and S is the scattering factor as before. Since I_0S is the same for the same substance and for the same incident radiation, we have taken its value to be 175 so that one of the points of the theoretical curve is made to coincide with the corresponding point on the experimental curve. $\phi(s)_{Ex}$ values have been compared with $\phi(s)_{Th}$ values for different values of μ according to the above formula in Fig. 1.

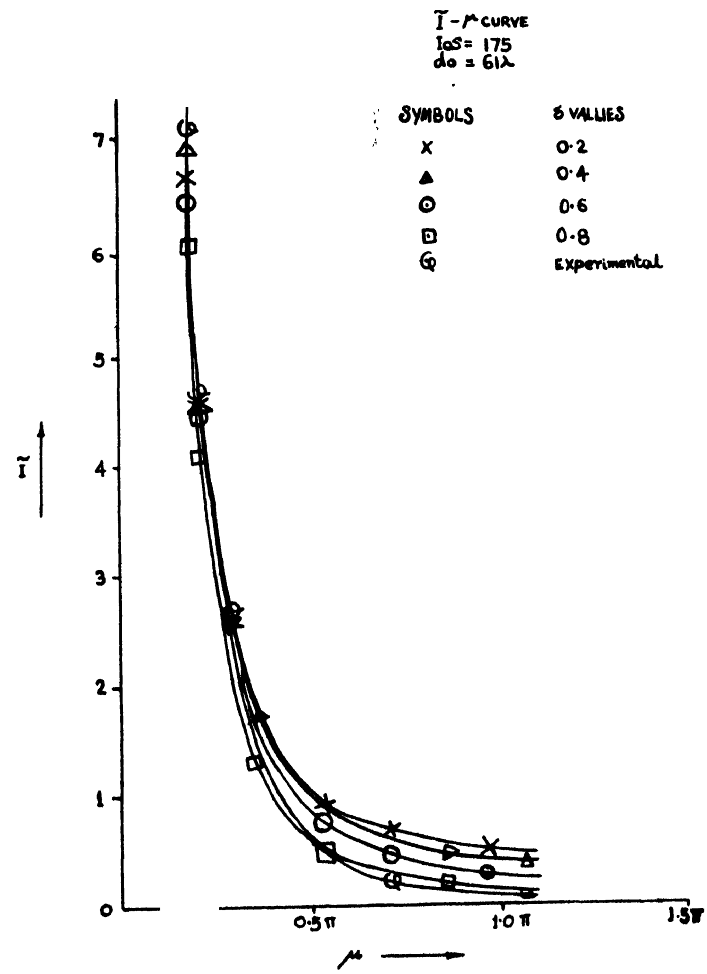

Fig. 1.

We have tried to get a good agreement between the theoretical and the experimental curves by taking four different values of δ, the relative fluctuation factor, as equal to 0.2, 0.4, 0.6 and 0.8 for a thickness factor of 61λ. For every one of these values the theoretical curves are drawn to the same scale in the same figure along with the experimental curve (Fig. 1, Table I). It is seen from the figure that when the mean thickness is 61λ there is good agreement between the theoretical and the experimental curves in the high intensity region if $\delta = 0.4$ and in the low intensity region when $\delta = 0.8$.

We have also tried to vary the thickness from 61λ to 40λ and 80λ. The theoretical $\phi(s)_{Th}$ values have been calculated and $\phi(s)_{Th}$ versus μ curves have been drawn for each one of them for the above four values of δ along with the experimental curve. These two sets of curves one for each thickness factor are not shown here. Drawn to the same scale with the same constant factor $I_0S = 175$ for the experimental curve, in none of these two cases there is found to be good agreement between the theoretical and the experimental curves.

TABLE 1

μ	$\phi(s)_{Th}$				$\phi(s)_{Ex}$
	$\delta = 0.2$	$\delta = 0.4$	$\delta = 0.6$	$\delta = 0.8$	
0.178	6.622	6.858	6.416	6.033	7.120
0.213	4.622	4.612	4.437	4.062	4.705
0.284	2.678	2.648	2.493	2.114	2.666
0.320	2.125	2.118	1.972	1.636	1.908
0.355	1.779	1.735	1.598	1.280	1.451
0.426	1.294	1.282	1.115	0.834	0.893
0.533	0.902	0.863	0.735	0.503	0.481
0.622	0.725	0.691	0.563	0.367	0.294
0.711	0.679	0.578	0.457	0.287	0.199
0.834	0.524	0.506	0.354	0.206	0.121
0.960	0.485	0.440	0.299	0.162	0.090
1.067	0.480	0.411	0.245	0.116	0.068

DETERMINATION OF RELATIVE DISTRIBUTION

It is seen that the relative fluctuation factor is 0.4 in the high intensity region and 0.8 in the region of low intensities corresponding to low and large angles of scattering respectively. It is wellknown that the inner part of the scattering curve is effected by the particles of large dimensions and the outer part of the scattering curve is effected by particles of small sizes. Again the principle of Statistical Independence after Landau (1958) demands that the relative fluctuation is inversely proportional to the square root of the number of particles in the macroscopic body, given by

$$\delta = \frac{\{\overline{(d-d_0)^2}\}^{\frac{1}{2}}}{d_0} \propto \frac{1}{N^{\frac{1}{2}}}$$

where N is the number of particles in the macroscopic body.

The agreement between the experimental and the theoretical curves of scattering is satisfacory on the inner parts when $\delta = 0.4$ Since the inner part of the curve is obviously due to large sized particles and since the value of δ is small, it means that N is large, i.e. the large sized particles are more in number. The outer part of the scattering curve corresponding to large angles is effected by particles of smaller dimensions. The very fact that a large value of $\delta = 0.8$ satisfies the outer region according to the above formula, N is small. In other words the number of layers corresponding to this region are small. That means the small sized particles are fewer in number. This amounts to saying that the large sized layers are more predominant. Thus the agreement of a large δ value in the outer region further supports the abundance of the large particles. Therefore it is very likely that the thicker layers are more predominant than the thinner ones.

It has been pointed out in a paper by one of us (Ratho, 1964) that there exists probably two types of layers of micelle of thickness of about 60 Å and 125 Å respectively. A rough relative distribution of layers can however be calculated from the above formula.

If N_1 is the number of thicker layers and N_2 the number of thinner layers and if δ_1 and δ_2 are the relative fluctuations for these two types of layers respectively, then from the above formula

$$N_1 = \frac{C}{\delta^2}$$

$$N_2 = \frac{C}{\delta_2^2}$$

where C is the constant of proportionality. Therefore the fraction of the thicker layers in the system is

$$\frac{N_1}{N_1+N_2} = \frac{\delta_2^2}{\delta_1^2+\delta_2^2}$$

Since $\delta_1 = 0.4$ is assigned to the thicker layer and $\delta_2 = 0.8$ to the thinner layers, we have

$$\frac{N_1}{N_1+N_2} = \frac{(0.8)^2}{(0.4)^2+(0.8)^2} = 0.80.$$

Therefore the thicker layers are predominant in the system, being about 80 %.

DISCUSSION

The effect of particle scattering on the total scattering can be shown to be negligible and our assumption that $\phi_1 = 0$ can hence be justified.

It can be easily seen from the expression

$$\phi_2 = \frac{\left(1-\cos\mu \cdot \cosh \mu^2 \frac{\delta^2}{2}\right)}{\left(\cosh \mu^2 \frac{\delta^2}{2} - \cos\mu\right)^2}$$

that for finite values of δ (which is always less than 1) the value of

$$\lim_{\mu \to 0} \phi_2 = \infty$$

In a paper by Porod (1949) it has also been shown that the particle scattering ϕ_1 can be given by

$$\phi_1 = \frac{1-k^2}{1-2k\cos\mu+k^2}$$

where $k = e^{-\mu^2\delta^2/2}$, $\mu = sd_0$ and δ is the relative fluctuation factor as before. Now it can be shown that

$$\lim_{\mu \to 0} \phi_1 = \delta^2 < 1$$

Therefore in the range of low angles of the order of 10^{-3} the effect of particle scattering on the total scattering, i.e. the effect of ϕ_1 on $\phi = (\phi_1 + 1/n\, \phi_2)$ is negligible.

CONCLUSION

The mean thickness factor is more than 90Å, as it is a densly packed system, this can be taken as the mean distance between the scattering centres. There are about 80%thicker layers in the sample. The particle scattering is negligible and the interparticle scattering is predominant.

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