Particle Size Determination of Polydisperse PVAc Latex by Light Scattering Measurement in Angular Sector between 0—90°

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By comparing the theoretical and experimental intensity ratios of vertical components of light scattered at the pairs of angles 40 : 30°, 45 : 35°, 50 : 40°, 60 : 45°, and 90 : 45° the average diameter of particles of polydisperse PVAc latex was estimated. The determined value was in agreement with the results of scattering ratio measurement and electron microscopy.

In this paper the possibility of estimating the average diameter of PVAc latex particles om the intensity ratio of the light scattered in two angles ranging from 0 to 90° has been ıvestigated. As a matter of fact, *Hodkinson* [1] pointed out that the distribution of the ght scattered in that angular sector might be employed as a convenient measure for ıe size of particles what is also obvious from Fig. 1. This figure shows the course of the ıtio of scattering intensities for selected pairs of angles depending on α according to the 'rauenhofer diffraction relationship [1]

$$i_1 + i_2 = 2\alpha^2[J_1(\alpha \sin \Theta)/\sin^2 \Theta], \tag{1}$$

ıhere $\alpha = \pi D/\lambda$ (D is the diameter of a particle and λ is the wave length of light in the ıedium under consideration), Θ and J_1 denote the angle of observation and Bessel ınction respectively, and i_1, i_2 are intensity functions (vertical and horizontal) published ı the tables of Mie scattering, *e.g.* [2]. The relationships $i_1(\Theta_1)/i_1(\Theta_2) = f(\alpha)$ are of similar haracter (Fig. 2) and have been calculated for $m = 1.10$ (relative refraction index f aqueous PVAc dispersions) on the basis of above-mentioned tables.

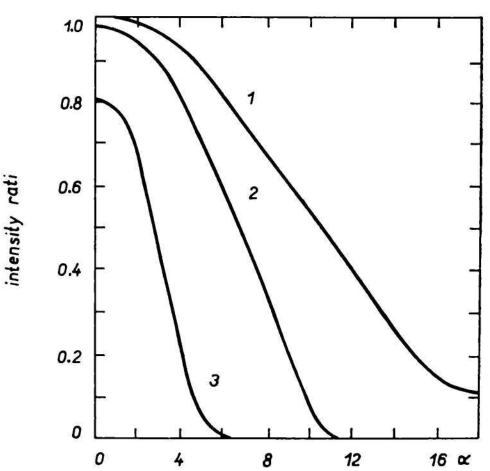

Fig. 1. Dependence on α of the intensity ratios for quoted pairs of angles according to the Frauenhofer diffraction [1].
1. 10 : 5°; *2.* 20 : 15°; *3.* 40 : 20°.

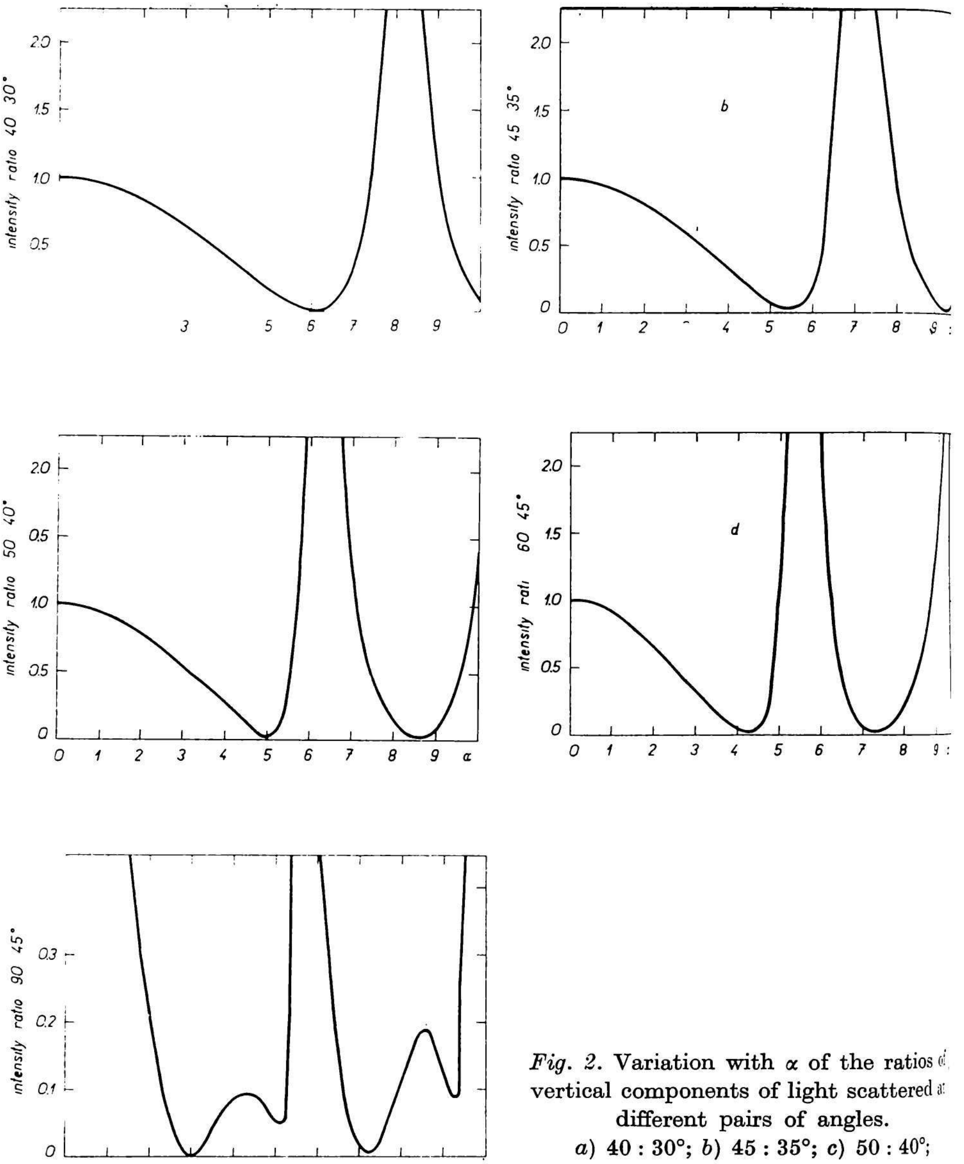

Fig. 2. Variation with α of the ratios of vertical components of light scattered at different pairs of angles.
a) 40 : 30°; *b*) 45 : 35°; *c*) 50 : 40°; *d*) 60 : 45°; *e*) 90 : 45°.

As evident from figures, an unambiguous reading of α allowing a comparison with the experimental results obtained for selected pairs of angles (considering experimental conditions) is possible only below $\alpha = 6$ approximately, at $i_{40°}/i_{30°}$. Provided the intensity ratios at several pairs of angles are taken into consideration, the multivalidity of data may be excluded for $\alpha > 6$.

Experimental

The latex under investigation was of similar origin as the material in paper [3], its weight average diameter $\bar{D}_w$ being 880 nm (determined by electron microscopy). The measurements of intensity of the scattered light with vertically polarized primary beam were made by the method described in [3], while the photometric data were corrected with respect to the volume observed (correction $\sin(\Theta)$).

Results and Discussion

Fig. 3 shows the variation of individual intensity ratios with concentration while the values $(I_{\Theta,1}/I_{\Theta,2})_0$ were found by extrapolating to zero concentration. These data are summarized in Table 1 where the corresponding values of α and D are also given. The

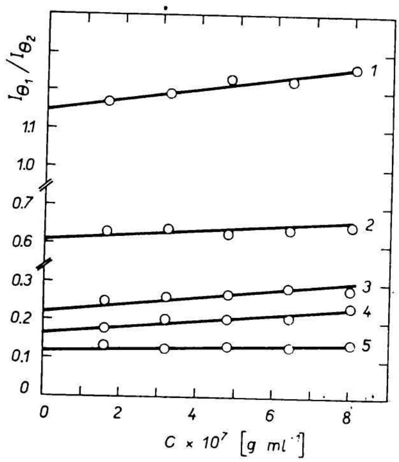

Fig. 3. Relationship between concentration and ratios of the vertical components of light scattered at different pairs of angles.
1. $\Theta_1 = 40°$, $\Theta_2 = 30°$; *2.* $\Theta_1 = 45°$, $\Theta_2 = 35°$; *3.* $\Theta_1 = 60°$, $\Theta_2 = 45°$; *4.* $\Theta_1 = 50°$, $\Theta_2 = 40°$; *5.* $\Theta_1 = 90°$, $\Theta_2 = 45°$.

arithmetic mean of the values was then used for the estimation of the particle diameter D. Thus it was found that $D = 1030 \text{ nm} \pm 3\%$. The values α were determined by comparing the corresponding results for all angle pairs and by eliminating inconvenient data.

As it was pointed out [3, 4], the scattering ratio σ is a convenient measure for the particle size of heterodisperse systems for $450 \text{ nm} < D < 2.800 \text{ nm}$ and $1.06 < m < 1.12$. On the basis of such measurements [3] the average diameter $\bar{D} = 1020$ nm was found for the latex investigated.

It is difficult to judge what average value is involved in the proposed method. As known, different methods of light scattering provide different average values of diameters and moreover each particular size distribution possesses its characteristic mean. For instance, the mean obtained by means of scattering ratio ought to be near to the weight average diameter [4]. After all, this fact is confirmed by the results of paper [4] which show a striking agreement with electron microscopic observation except a single case in which light scattering gave the value $\bar{D} = 1160$ nm and electron microscopy $\bar{D} = 920$ nm for PVAc latex. As evident, the results of this investigation as well as the results presented in our preceding paper [3] ($\bar{D}_{EM} = 980$ nm and $\bar{D}_{LS} = 1.180$ nm) are of similar character. It is, however, noteworthy that this agreement is very good in view of experimental errors.

Table 1

Diameters of the particles of polydisperse PVAc latex obtained at different pairs of angles

Θ_1/Θ_2	40°/30°	45°/35°	50°/40°	60°/45°	90°/45°
$(I_{\Theta,1}/I_{\Theta,2})_0$	1.14	0.61	0.16	0.22	0.12
$(I_{\Theta,1}/I_{\Theta,2})_0 \cdot (\sin \Theta_1/\sin \Theta_2)$	1.47	0.75	0.31	0.27	0.17
α	7.6	8.1	7.7	8.0	8.3
$\bar{D}$ [nm]	990	1060	1000	1040	1080

In the presented method neither the mathematic formulation of the problem (relationship (*1*)) nor the plot $i_1(\Theta_1)/i_1(\Theta_2) = f(\alpha)$ allows to determine the character of the mean. Then only on the basis of the agreement with the results of electron microscopy and scattering ratio the mean obtained may be considered a weight average.

According to Fig. 2 the relationship $i_1(\Theta_1)/i_1(\Theta_2) = f(\alpha)$ shows an oscillating character. The same effect may also be observed with the relationship $z = I(45°)/I(135°) = f(\alpha)$, where z and I denote the dissymmetry coefficient and the intensity of light scattered in relevant angles, respectively [3, 5]. As shown in paper [3], the multivalidity of data was eliminated by measuring the dissymmetry coefficient in nonpolarized or vertically and horizontally polarized primary beam.

Finally, it may be stated that the application of the Frauenhofer diffraction relationship to the determination of the particle diameter of current PVAc latices principally requires the possibility of measuring the scattered light at low angles, for instance 20 and 15°. Provided there are data for several pairs of angles available, then the angle range between 30 and 90° may be used for the determination of particle size. As it was shown, the results of such measurements were in excellent agreement with those obtained by measuring the scattering ratio (intensity ratio of the light scattered using horizontally and vertically polarized primary beam), *i.e.* by the measurements of different character. It is worth noting that the proposed method involves the relationships principally valid for monodisperse systems.

References

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