Particle Size Determination of Polydisperse Latex by Light Scattering

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The applicability of simple transversal light scattering methods for particle size determination of polydisperse emulsion has been investigated. By the study of PVAc latex with weight average diameter of 980 nm the minimum intensity, dissymmetry and scattering ratio methods were applied, always with the use of Mie's theory. The measurements were carried out on photogoniodiffusometer Sofica, which in principle is without reflexions. In agreement with theoretical assumptions, the depolarization measurements gave a higher, dissymmetry a lower value of diameter in comparison with D_w. The method of minimum intensity proved to be unsuitable. The theoretical values of dissymmetry for $m = 1.10$ and $\alpha = 0(0.2)10.0$ for a nonpolarized, vertically and horizontally polarized primary beam were also calculated.

Both for research and for practice the size determination of particles of colloidal dispersions is of fundamental importance. When particles are hard, unable to undergo deformation, electron microscopy can be successfully applied. In other cases indirect methods must be used. Among these, the foremost place hold the methods of light scattering as described by *Sedláček* [1]. In our paper for the size determination of particles of PVAc latex, the following measurements of light scattered intensity were used: method of minimum intensity, dissymmetry and depolarization measurements, always with the application of Mie's theory [2].

In the dissymmetry method the coefficient of dissymmetry z is defined by the relation $z = I_{45°}/I_{135°}$, where I means the intensity of light scattered in two angles. On the basis of Mie's theory z is the function of m and α, where m is the ratio of refractive index of scattering particles and medium in which they are dispersed and $\alpha = \pi D/\lambda$; here D is the diameter of particles and λ the wavelenght of light in the medium. The value of z can be calculated with the use of suitable tables (see further) for the different combinations of m and α. By comparison of theoretical dependences thus obtained with the measured value of z it is possible to calculate the diameter of particles D.

In agreement with Mie's theory, the relative intensity of scattered light I_Θ (with respect to the primary beam of intensity I_0) is the function of angle Θ. This dependence can show minima and maxima, the number and situation of which is the function of m and α. *Pierce* and *Maron* [3] pointed out the possibility of calculating the size of particles on the basis of such dependences. In case only minima are studied, we speak of the method of minimum intensity.

Light scattered by an isotropic spherical particle in an angle $\Theta = 90°$ in a nonpolarized primary beam is fully linearly polarized when $\alpha \to 0$. For greater values of α scattered light is only partially polarized and the degree of polarization can be the criterion of size of spherical particles. There are two ways of expressing quantitatively the degree of polarization [4]:

1. By depolarization $\Delta = I_1/I_2$, where I_1, I_2 are the components of intensity of scattered light in a nonpolarized primary beam. I_1 is parallel with the plane of observation, I_2 is vertical to it.

2. By scattering ratio $\sigma = I_h/I_v$, where I_h, I_v are the intensities of scattered light by a horizontally or vertically polarized primary beam. For spherical particles, however, is valid $\Delta = \sigma$ and, therefore, taking into consideration experimental conditions it is possible to choose either Δ or σ measurements. Since the theoretical value of σ (for given m) can, on the basis of tabular values I_h, I_v [5], be calculated for various α, in comparison with the experiment the sought for size of particles can be determined.

Experimental

As material was used polyvinylacetate latex, product of W. Pieck Chemical Works, Nováky, Czechoslovakia. The original 50% latex was diluted with redistilled water to 0.5% solution which was centrifuged for 20 minutes at 400 G for the purpose of removing possible aggregates. By means of a pipette 20 ml of the emulsion were removed or 20 g were weighed and then by evaporation and drying in a vacuum drier at a temperature of 60°C to a constant weight, the polymer concentration was determined. A series of further dilutions of centrifugated latex was prepared by volume using pipettes or measuring flasks.

To calculate the index of refraction of scattering particles the following relation was used [6]:

$$n = n_0 + \frac{\mathrm{d}n}{\mathrm{d}c} \cdot \varrho ,$$

where n_0 is the refractive index of the solvent, ϱ the density of the material and $\mathrm{d}n/\mathrm{d}c$ the refractive index increment. From the latex a film was prepared which was dissolved in dimethylformamide and the refractive index increment was determined by means of an interferometer (Zeiss, Jena). Using literature data [7] for density $\varrho = 1.19 \times 10^3$ kg m^{-3} the relative refractive index was calculated $m = 1.105$, which is in agreement with data in paper [6].

Light scattering measurements were made on photogoniodiffusometer (Sofica, Paris) both with a polarized and a nonpolarized primary beam ($\lambda_0 = 546$ nm) under normal conditions.

The optical purity of water used was controlled by measuring the reduced intensity of scattered light, where the measured value $R_{90} = 1.24 \times 10^{-6}$ was in agreement with data $R_{90} = 1.25 \times 10^{-6}$ given by *Kratohvil* [8].

To determine the angle of minimum intensity the vertical component was not measured as in [9], but the total intensity of scattered light in a nonpolarized primary beam in the range 40—135°. *Maron et al.* [10] have pointed out the possibility of such measurements. The actual intensities of scattered light thus observed in the given angles must be corrected by volume correction. The correction was made by multiplying the reading of the photometer with sin (Θ). In evaluating the results the dependence of intensities $1/I_\Theta$ on $\sin^2 (\Theta/2)$ thus corrected was plotted.

In the dissymmetry method the dependence $1/z - 1$ on concentration was graphically represented and the data were extrapolated to zero concentration. The dissymmetry was measured in a nonpolarized, vertically or horizontally polarized primary beam. In the following, the value z_0 obtained by extrapolation was compared with the theoretical value.

The state of polarization of light, scattered by the latex under investigation, was determined by the measurement of scattering ratio. The dependence $\sigma = f(c)$ was extrapolated to zero concentration and the value σ_0 was obtained.

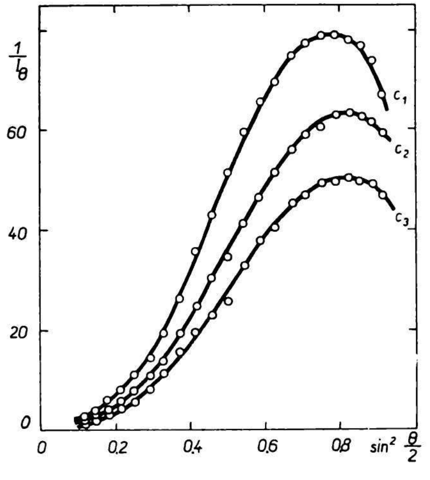

Fig. 1. Radiation envelope of PVAc latex for three concentrations: $c_1 = 1.66 \times 10^{-7}$; $c_2 = 2.90 \times 10^{-7}$; $c_3 = 4.14 \times 10^{-7}$ g ml^{-1}.
$1/I_\Theta$ in arbitrary units.

Results and Discussion

The results of paper [10] pointed out the fundamental applicability of the method of minimum intensity to determine the average diameter of particles also in polydisperse butadiene—styrene latices with average weight diameter $D_W = 328$ or 392 nm. PVAc latex in our work had $D_W = 980$ nm (determined by an electron microscope); the dependence $1/I_\Theta$ on $\sin^2 (\Theta/2)$ is in Fig. 1. The curves show but one maximum, which, considering the relatively high value of α is improbable. Therefore, on the basis of tables [5] the theoretical values of $1/I_\Theta$ were calculated for $m = 1.10$ and $\alpha = 7.8$ ($D = 1000$ nm) and their dependence on $\sin^2 (\Theta/2)$ can be seen in Fig. 2. In comparing the theoretical and experimental dependence it is seen that in the system under investigation the radiation envelope observed is obviously the sum of contributions from the individual particles of various size, so that oscillations in dependence of intensity on the angle of observation were not found. To evaluate the significance of a single intensity minimum is controversial. However, it is necessary to note that if it is considered as the minimum of the fourth order, then on the basis of the relation

$$\frac{D}{\lambda} \sin \frac{\Theta_{\min}}{2} = k_4$$

and k_4 calculated according to *Pierce* and *Maron* [3], for $\Theta_{\min} = 120°$ (found by extrapolation to zero concentration) $D = 1030$ nm.

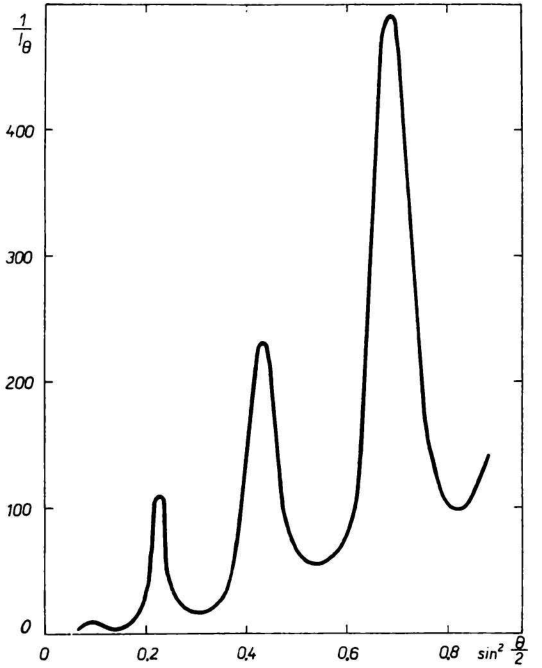

Fig. 2. Theoretical radiation diagram of system with spherical particles ($m = 1.10$, $\alpha = 7.8$). $1/I_\Theta$ in arbitrary units.

In paper [11] it is stated that measurements of dissymmetry for the purpose of determining the size of particles of polydisperse latices are not sufficient. Since in the mentioned paper were investigated latices up to the size $D_w = 250$ nm, it was examined to what extent the above mentioned had relation to our latex. The extrapolated value $z_0 = 20.8$ was compared with the theoretical value on the basis of the diagram $z = f(\alpha)$, constructed according to Table 1. The table values were calculated according to the relation

$$z = \frac{(i_1 + i_2)_{45}}{(i_1 + i_2)_{135}},$$

where values i_1, i_2 for $m = 1.10$ and various α are given by scattering functions of spherical particles [5]. This comparison can also be made on the basis of dependence published in [12], however, the interpolation is less accurate in comparison

Table 1

The values of dissymmetry z_{45} at $m = 1.10$

α	z_{45} a	b	c
0.2	1.0238	1.0206	1.0245
0.4	1.0993	1.0979	1.1022
0.6	1.2395	1.2359	1.2470
0.8	1.4730	1.4647	1.4895
1.0	1.8585	1.8411	1.8940
1.2	2.5259	2.4879	2.6035
1.4	3.7907	3.7016	3.9766
1.6	6.5648	6.3227	7.0864
1.8	14.289	13.433	16.256
2.0	48.402	43.124	62.753
2.2	588.06	428.39	1889.1
2.4	231.40	262.44	190.57
2.6	59.340	60.921	56.706
2.8	24.806	33.797	36.743
3.0	29.989	27.652	35.178
3.2	34.416	29.847	46.699
3.4	53.648	42.846	93.328
3.6	132.91	93.385	442.36
3.8	679.90	440.41	5622.6
4.0	215.24	229.64	195.89
4.2	53.924	47.214	68.820
4.4	24.096	18.769	41.003
4.6	14.672	10.453	32.468
4.8	11.256	7.3636	32.187
5.0	11.084	6.5292	41.948
5.2	15.940	7.9079	94.634
5.4	27.100	10.415	385.81
5.6	9.0260	3.7511	46.549
5.8	4.9777	2.7362	18.134
6.0	5.2307	3.4033	15.089
6.2	7.4913	5.2727	18.564
6.4	13.665	10.024	30.569
6.6	34.069	25.456	72.881
6.8	134.99	95.732	389.18
7.0	219.35	138.27	3169.2
7.2	75.020	52.397	232.58
7.4	39.891	28.795	98.433
7.6	30.366	22.061	70.651
7.8	29.964	21.682	68.995
8.0	38.047	27.299	87.613
8.2	67.191	47.706	153.41
8.4	165.41	110.08	473.88
8.6	96.555	54.570	1163.7
8.8	24.780	13.731	170.49
9.0	9.5439	5.0289	49.366
9.2	5.1956	2.4904	22.839
9.4	4.1825	1.8318	15.481
9.6	6.0270	2.9123	16.543
9.8	17.223	10.937	31.949
10.0	49.117	29.453	163.83

a — unpolarized, b — vertically, c — horizontally polarized primary beam.

with the application of Table 1. From the comparison of the theoretical and experimental dependence $z = f(\alpha)$, there follows for α in the work under consideration seven valid data. Because of the electron optic value 980 nm, only two data have come under consideration: $\alpha = 6.5$ and 8.8 or $D = 850$ and 1150 nm. Since there were at our disposition also values of dissymmetry in a vertically or horizontally polarized primary beam, the same as in the preceding, these were compared with the theoretical values given in Table 1. For the comparison of $z_0 = 16.9$ (a vertically polarized primary beam, see Fig. 3), there follow now five data from which also $\alpha = 6.5$ and 8.8. For horizontally polarized light, the value $z_0 = 33.8$ was obtained by extrapolation, which from the given data confirmed now only the value $\alpha = 6.5$.

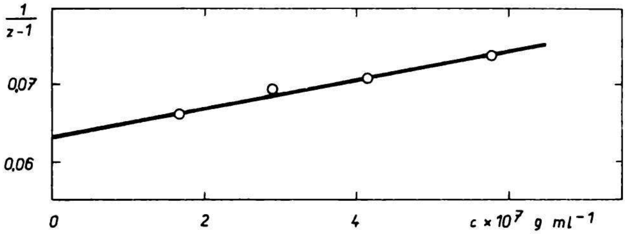

Fig. 3. Concentration dependence of dissymmetry at vertically polarized primary beam.

In connexion with the determination of the diameter of particles on the basis of the measurement of scattering ratio, the extrapolated value $\sigma_0 = 0.178$ (see Fig. 4) was compared with the theoretical value on the basis of the dependence $\sigma = f(\alpha)$ for $m = 1.10$ plotted on the basis of data already published [13]. Likewise, as in dissymmetry, here also several valid data for α were obtained, among others also $\alpha = 7.6$ and 8.8.

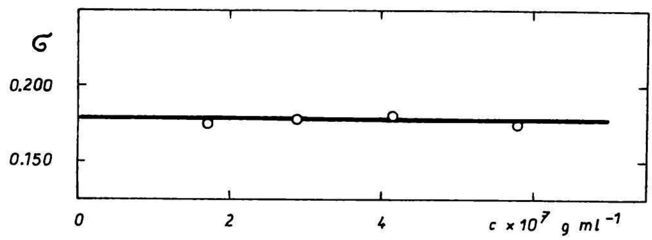

Fig. 4. Concentration dependence of scattering ratio.

Graessley and *Zufall* [6] suggested the theoretical dependence $\bar{\sigma} = f(\alpha)$ for various m, where $\bar{\sigma}$ is linearly dependend on α. In comparing the experimental value with this dependence, it was found that $\alpha = 9.1$. With this value corresponds

$$D = \frac{\int_0^\infty D^{7/2}\, N(D)\, \mathrm{d}D}{\int_0^\infty D^{5/2}\, N(D)\, \mathrm{d}D} = 1180\ \text{nm},$$

where $N(D)\,\mathrm{d}D$ is a fraction of particles with diameters in the interval D and $D + \mathrm{d}D$.

As can be seen, the results are, as a whole, in good agreement. Taking into account that which has already been given, in contradiction with conclusions of paper [10], the method of minimum intensity, however, cannot be recommended for studying heterodisperse systems with particles with a relatively large average diameter. In connexion with method of dissymmetry, it is necessary to emphasize that work was carried out with an apparatus which basically worked without reflection effects. Hereby the importance of proper correction is pointed out in the presence of such effects. Their negligence, or improper correction of results can have very serious consequences [14]. The lower value of D from the measurement of dissymmetry in comparison with D_w can be explained on the basis of results from paper [11]. Here for polydisperse latex $D_w = 247$ nm and when $\lambda = 409.4$ nm, it was found that $D = 223.0$ nm and when $\lambda = 519$ nm, $D = 264.0$ nm. Likewise, according to paper [15] large particles ($\alpha > 1.9$) show a decrease of dissymmetry with growing diameter when $\lambda_0 = 436$ nm, but not when $\lambda_0 = 546$ nm. That is why dissymmetry and the corresponding calculated sizes with 436 nm were lower in comparison with data for $\lambda_0 = 546$ nm. Further conclusions have not been made because dissymmetry measurements at various wavelenghts in our case, have not been made for experimental reasons.

Concerning diameter D from depolarization measurements, it must be stated that its higher value, in comparison with D_w is in agreement with the experimental results of other authors [6, 15]. The main cause is obviously the different average diameter considered in depolarization or electron microscopic measurements.

As can be seen, the dissymmetry method together with the measurement of depolarization are suitable for evaluating the average diameter of heterodisperse polyvinylacetate latices.

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